PB89-155220

Quality Assurance Support for the National Atmospheric Deposition Program and National Trends Network Monitoring Activities: 1987-1990. Interim Report

Colorado State Univ., Fort Collins

Prepared for

Environmental Protection Agency
Research Triangle Park, NC

Feb 89

U.S. Department of Commerce
National Technical Information Service
NTIS

PB89-155220

EPA/600/3-89/012
February 1989

Interim Report: Quality Assurance Support for the National Atmospheric Deposition Program and National Trends Network Monitoring Activities: 1987-1990

Grant Number CR813910-02

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SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA/600/3-89/012	2.	3. RECIPIENT'S ACCESSION NO. [illegible]9 155220/AS
4. TITLE AND SUBTITLE Interim Report: Quality Assurance Support for the National Atmospheric Deposition Program and National Trends Network Monitoring Activities: 1987-1990		5. REPORT DATE February 1989
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) David S. Bigelow		8. PERFORMING ORGANIZATION REPORT NO. NA
9. PERFORMING ORGANIZATION NAME AND ADDRESS Natural Resource Ecology Laboratory Colorado State University Ft. Collins, Colorado		10. PROGRAM ELEMENT NO. CCVN1A
		11. CONTRACT/GRANT NO. CR 813910-02
12. SPONSORING AGENCY NAME AND ADDRESS U.S. Environmental Protection Agency Atmospheric Research and Exposure Assessment Laboratory Quality Assurance Division Research Triangle Park, North Carolina 27711		13. TYPE OF REPORT AND PERIOD COVERED
		14. SPONSORING AGENCY CODE EPA/600/09

15. SUPPLEMENTARY NOTES

16. ABSTRACT

This report summarizes the quality assurance activities of the NADP/NTN network from mid-1987 through mid-1988. The report presents some accomplishments and makes recommendations for the network.

The report discusses data quality issues relating to site representativeness, field versus laboratory measurements of pH, site operator turnover rates and various monitoring network reviews. The report also contains the previously released "NADP/NTN Instruction Manual for Site Operation" and the "Quality Assurance Report of NADP/NTN Deposition Monitoring for Laboratory Operations" as well as an NADP/NTN quality assurance bibliography.

Recommendations emphasize the role ofthe quality assurance manager in coordinating quality assurance activities, the need for more integrated quality assurance evaluations, the need to standardize quality assurance data reporting formats and data transfer protocols in the network and the need for establishing a method for estimating overall precision and accuracy in spatial and temporal data summary statistics.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES 309 344
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

DISCLAIMER

Preparation of this report has been funded in part by the U.S. Environmental Protection Agency under Grant No. CR813910-02 to Colorado State University. It has been subjected to the Agency's peer review and administrative review and it has been approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

ABSTRACT

This report summarizes the quality assurance activities of the NADP/NTN Quality Assurance Manager from mid-1987 through mid-1988. The report presents some accomplishments and makes recommendations for the network.

The report discusses data quality issues relating to site representativeness, field versus laboratory measurements of pH, site operator turnover rates and various monitoring network reviews. The report also contains the previously released *NADP/NTN Instruction Manual for Site Operation* and the *Quality Assurance Report of NADP/NTN Deposition Monitoring for Laboratory Operations* as well as an NADP/NTN Quality assurance bibliography.

Recommendations emphasize the continued support of the quality assurance manager's role in coordinating quality assurance activities, the need for more integrated quality assurance evaluations, the need to standardize quality assurance data reporting formats and data transfer protocols in the network and the need for establishing a method for estimating overall precision and accuracy in spatial and temporal data summary statistics.

This report was submitted in fulfillment of Grant No. CR813910-02 by Colorado State University under the partial sponsorship of the U.S. Environmental Protection Agency.

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SECTION 1
INTRODUCTION

Background

The National Atmospheric Deposition Program (NADP) monitoring network began operations in July of 1978. The Network used, and continues to use cooperating local, state and federal agencies as well as private industry to operate a network of sites according to a single set of protocols. In 1983, NADP assumed responsibility for managing the day-to-day operations of the the National Acid Precipitation Assessment Program's National Trends Network (NTN). This action resulted in the combined, cooperative monitoring program now known as the NADP/NTN monitoring network (Cowling et al., 1977; NADP, 1978; Interagency Task Force On Acid Precipitation, 1982; Robertson and Wilson, 1985). The NADP/NTN monitoring network serves both the National Atmospheric Deposition Program and the National Acid Precipitation Assessment Program.

Because the NADP/NTN monitoring program both represents and relies on many different public and private agencies to accomplish its goals, it is unique in its structure and mode of operation (NADP, 1984). For quality assurance, this has meant that responsibility for the development of quality assurance programs has been and continues to be a voluntary effort assumed by each of the agencies who have responsibility for managing specific pieces of the network operations (i.e Field Sites, Central Analytical Laboratory, Coordination Office, U.S. Geological Survey, U.S. Environmental Protection Agency). These quality assurance procedures are then reviewed and accepted by the various NADP committees who have responsibility for overseeing each network function. This practice has been strongly encouraged since it would require considerable effort and expertise to centralize this function within a single organization.

A decentralized approach to quality assurance, however, creates its own problems. Many of the network quality assurance procedures are innovative adaptations of recognized quality assurance practices, and as such are reported in the scientific literature, at professional and technical meetings or in various agency reports rather than in a standard network document or operating procedure publication (see Selected Publications). This lack of centralized quality assurance reporting makes documenting the achievement of network data quality goals and objectives difficult and also makes it difficult to continue some key quality assurance programs once scientific recognition for the techniques has been achieved. The likelihood that those quality assurance activities that cannot be maintained by a single agency, either because of financial or cooperative restraints, will be overlooked is also increased. Finally, decentralized reporting can lead to situations where results from one effort may conflict with another such that no clear picture of 'true' data quality can emerge.

Recognizing the need for a more coordinated and thorough quality assurance program, NADP formed a study committee, in 1982, to address this issue. The work of this committee resulted in the development of a Quality Assurance Plan (NADP, 1984) to cover all aspects of network operation and the recommendation that a full time Quality Assurance Manager be appointed to administer this quality assurance program. The desirability of a coordinated quality assurance program was again recognized in the NAPAP Peer Review held in Boulder, Colorado in 1985 (Joyner, 1986)

Objectives

The purpose of the cooperative agreement, *Support To The National Atmospheric Deposition Program/ National Trends Network Quality Assurance Program*, contract number CR813910-02, is to provide on-going support for the NADP/NTN Quality Assurance Manager. The QA Manager coordinates the quality assurance activities of the joint NADP/NTN monitoring network, identifies and develops new quality assurance programs for the network as necessary, and reports on the quality of deposition data being produced by the NADP/NTN monitoring effort.

It is the responsibility of the Quality Assurance Manager to administer the NADP Quality Assurance Plan that was adopted by the NADP program in 1984. This requires the Manager to maintain close liaison with the Central Analytical Laboratory; the U.S. Geological Survey's external NADP/NTN audit programs; the data management and publication activities of the NADP/NTN, as administered through the Coordinator's Office; the EPA's Site Visitation Program and Acid Deposition System for Statistical Reporting (ADS); and to establish a program to monitor the activities at each of the deposition monitoring stations. The QA Manager also works closely with the QA Steering Committee and provides necessary information to appropriate NADP and NAPAP Task Group IV committees. The Manager is independent of other program operations, such as network site operations, chemical analysis, data management and publication.

The primary objectives of the Quality Assurance Manager are to:

1 Oversee the implementation of the NADP Quality Assurance Plan.
2. Review and recommend changes to the NADP/NTN monitoring network's, field operations, laboratory operations, data management and external quality assurance programs and activities.
3. Identify and evaluate the type, level, and effectiveness of the quality assurance procedures in each phase of the program.
4. Report the results of these evaluations.
5. Provide centralized documentation of the quality assurance activities, both internal and external to the program.
6. Troubleshoot the weaknesses and future needs of the NADP/NTN quality assurance program; take action to correct the problems and meet the future needs of the program.
7. Maintain and prepare documents outlining the details of the NADP/NTN quality assurance procedures.

SECTION 2
ACCOMPLISHMENTS

Coordination of NADP/NTN Quality Assurance Plan Implementation

The primary coordination efforts have involved attending the frequent NADP Technical and Subcommittee meetings; writing, revising and reviewing NADP/NTN documentation; reviewing agency reports and proposals that utilize NADP/NTN data or documentation; and disseminating quality assurance information to the various NADP committees and scientists. Each of these activities serves as a vehicle for obtaining and documenting the quality assurance activities of the network and for promoting the evaluation and reporting of quality assurance data.

An additional part of the coordination effort has involved overseeing the Site Visitation Program and providing administrative assistance to the program's auditors. The Quality Assurance Manager is responsible for distributing the results of the site audits and for initiating corrective action to correct any discovered deficiencies. As with all of the external quality assurance programs, results are reported separately by each sponsoring agency.

Review and Revision of the NADP/NTN Quality Assurance Plan

During October of 1986 the NADP Quality Assurance Steering Committee began the task of reviewing and revising the NADP Quality Assurance Plan. As a part of this process, external reviewers were asked to make suggestions to improve the plan. By 1987 reviewer comments had been received and assignments made for revising all portions of the Plan. This process continues with the Quality Assurance Manager taking a lead role in the development of the Data Management portion of the Plan. A first revised working draft was completed in August of 1988.

As a part of this revision and in response to reviewer comments a Remedial Action Plan (RAP) was developed for correcting instances of non-compliance detected during network operations. The RAP was completed and approved in November 1987. It outlines for the first time the responsibilities of the subcommittees and program managers for resolving network deficiencies. Section 5 contains the approved NADP/NTN Remedial Action Plan.

Review and Evaluation of NADP/NTN Network Operations

Four areas of Network operations were targeted for review during the past contract year by the Quality Assurance Manager. The reviews covered regional representativeness of NADP/NTN monitoring data, differences between NADP/NTN laboratory and field data, turnover rates of NADP/NTN site operators and the review and revision of the 1982 site operator's instruction manual. The reviews resulted in the presentation of two scientific papers[1] [2] (See Sections 6), the drafting of two formal reports to the NADP Technical Committee[3] [4] (See Section 7) , the publication of a revised instruction manual for site operations[5] (Section 8) and the preparation of one journal article[6].

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[1] BIGELOW, D.S., 1987. ***Regional Influences On Siting And Sampling In The National Atmospheric Deposition Program/ National Trends Network Monitoring Program.*** Presentation at the European Monitoring and Evaluation Programme (EMEP) Workshop On Data Analysis And Presentation, Cologne, West Germany, June 15-17, 1987.

[2] BIGELOW, D.S., 1987. ***An Evaluation Of Representativeness Of Precipitation Volumes Measured In The National Atmospheric Deposition Program/ National Trends Network Monitoring Program.*** Presentation no. 271, 29th Rocky Mountain Conference, Symposium On Quality Assurance, Denver, Colorado, August 2-6, 1987.

[3] Sisterson, D.L., BIGELOW, D.S., Malo, B.A., and Stensland, G.J., 1987. ***A Study Of The National Atmospheric Deposition Program Field Versus Laboratory pH Differences.*** Report made to NADP Technical Committee November 1987.

Regional Representativeness

The representativeness of NADP/NTN monitoring stations has been and continues to be a difficult issue for data analysts. Indicators have been developed, such as the NADP/NTN, Acid Deposition System [(ADS) Watson and Olsen, 1984], Unified Deposition Data Base Committee [(UDDBC) 1986] completeness criteria and the UDDBC site ratings, to reduce some of the uncertainty associated with variations in site performance and emission profiles. Spatial analysis techniques such as Kriging are being applied to deposition data in an attempt to reduce uncertainties associated with deposition estimates at both sampled (sites) and unsampled locations. In spite of these efforts the evaluation of representativeness continues to be specific to the particular use to which the data will be applied. Since the data from the NADP/NTN monitoring program has wide application in many scientific disciplines and on various spatial and temporal scales (e.g. local, regional, continental, monthly, annually, etc) representativeness can only be addressed from a network quality assurance basis through the documentation and classification of sites according to regional discriminators. These discriminator's however, are only useful for identifying reasons for *unrepresentativeness.* Statistical techniques, such as those employed by Patrinos, et al (1979), Huff (1969,1971), and Nappo et al (1982, 1983), or, data set selection that meets assumptions of randomness, should be chosen and applied when assumptions of representativeness are required. See also Sections 6 and 9.

The NADP/NTN Quality Assurance Manager continues to provide the ADS data system with site ratings for NADP/NTN monitoring stations according to the rules developed by the UDDBC. The last comprehensive evaluation was done in March of 1986 and included NADP/NTN sites in operation as of 1985. Periodic updates have been provided upon request. The ratings appear in the Annual ADS summaries of *Acid Precipitation in North America* (EPA 600/4-85/061, EPA 600/4-86/033, EPA 600/4-87/035).

Field verses Laboratory pH Measurements

The reasons for differences between field and laboratory pH measurements in the NADP/NTN monitoring program have been discussed at numerous NADP Technical Committee meetings. Bucket contamination, poor quality field measurements, chemical and microbial decomposition as well as the absorption of gaseous species have all been discussed as potential sources of the differences. In response to a specific proposal to eliminate field pH and conductance measurements from the NADP/NTN monitoring program, differences between the two measures of pH were examined using 1984-1986 external quality assurance data from the U.S. Geological Survey's Blind-Audit and Intersite comparison programs (Brooks et al. 1987, 1988; Schroder et al. 1985, 1987; See et al. 1988), quality control data from each of the monitoring sites and internal laboratory quality control bucket-blank data. Results indicate a negative bias in hydrogen ion concentration measurements reported by the laboratory. The bias has a fixed component, associated with the bucket and lid, of about 8 μeq/L, and a seasonal and regional component that ranges from approximately +4 to -22 μeq/L at the 10th and 90th percentiles. The median difference between field and laboratory pH values, expressed as hydrogen ion concentration, in network data in 1984 through 1986 was -4.6 μeq/L. At a pH of 4.6, the overall, weekly, median, Network value, this difference represents an 18% bias. For many eastern sites

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[4] Simmons, C., Still, M.E., Stensland, G.J. and BIGELOW, D.S., 1987. ***Observer Turnover In The NADP/NTN Network: Implications For Training.*** Report to the NADP Technical Committee, November 2-5, 1987.

[5] BIGELOW, D.S. and Dossett, S.R. 1988. ***NADP Instruction Manual: Site Operations.*** National Atmospheric Deposition Program, Natural Resource Ecology Laboratory, Colorado State University, Ft. Collins, CO. April 1988.

[6] BIGELOW, D.S., Sisterson, D. L. and Schroder, L.J. 1988. ***An Interpretation of Differences Between Field and Laboratory pH Values Reported by the National Atmospheric Deposition Program.*** Submitted to Environmental Science and Technology, August 1988.

the bias would be less. However, for western sites the bias may mean that [H^+] are actually a factor of two higher than reported. Results of this study have been submitted to a scientific journal and are therefore not included in this report[6].

Operator Turnover Statistics

The NADP/NTN Quality Assurance Plan states that field observations are to be made by *trained* site personnel. To meet this requirement the program provides site operators with the opportunity to obtain training at the Central Analytical Laboratory (CAL) at the Illinois State Water Survey. Initials of reporting parties completing the network's Field Observer Reporting Forms were compared to operator training records to determine what portion of the data collected was in fact being forwarded by a trained site operator and to determine if the frequency of training offered was adequate to sustain the requirements of the program.

Results indicated that the number of observers at sites can range from 1 to 38 in a two year time period. Most all sites had more than one observer at any given time and over half of the listed observers made fewer than 12 observations during the two year time period studied. The surprising turnover in site personnel at many sites caused the training capacity of the program to be exceeded by approximately 100 people in each of the two years studied. The report also noted however that only 15% of the observations were made by untrained operators. See Section 7.

Revision of the NADP/NTN Site Operator Manual

During 1987 the NADP/NTN Site Operation Manual was reviewed and extensively revised. Revisions included approximately 50 additional pages of troubleshooting guidelines for the Aerochem Metrics and Belfort Rain gage and integrated documentation for changes that have occurred in field protocols over the course of the program. Field laboratory procedures were also revised to reflect the standardization of the pH electrode which took place in 1984. See Section 8.

Peer and Management Review of the NADP/NTN Monitoring Program

In April of 1988 the Quality Assurance Manager presented an overview and report of NADP/NTN quality assurance activities to a peer review panel organized at the request of NAPAP's Task Group IV on Deposition Monitoring. The written report furnished the reviewers is available through the NAPAP headquarters in Washington, DC.

A management review of the NADP/NTN monitoring program was conducted in August of 1988 by representatives of the National Acid Precipitation Assessment Program's Task Group on Deposition Monitoring (the U.S. Geological Survey) and the U.S. Department of Agriculture's Cooperative State Research Service (CSRS). The review was split into two parts, one at the NADP/NTN Coordination Office and the other at the contract laboratory at the Illinois State Water Survey. The review focused on the schedule and approach to meeting the deliverables that are outlined in each agencies contract with the reviewed parties.

The review was positive and 1) noted that the Coordination Office was fully staffed, 2) recommended an additional position to track site visitation reports and implement remedial action as outlined in the newly approved remedial action plan, 3) noted that all deliverables were being furnished on time with the exception of a laboratory quality assurance plan and 4) noted considerable progress in reducing data turn-around since the last review. Reviewers took note of the improvements in the program which had resulted from the previous review. Working documents used during the review are available upon request through the NADP/NTN Coordination Office.

Unified Deposition Data Base Committee and ASTM

The Quality Assurance Manager continues to participate in the Unified Deposition Data Base Committee (UDDBC) (a United States/ Canadian scientific committee involved with producing quality assured deposition data for North America) and in ASTM. Involvement in these groups has focused on identifying common techniques for determining the regional representativeness of monitoring stations, identifying techniques for determining precision and accuracy of seasonal wet deposition estimates, standardizing the treatment of low volume events in data summarization techniques and developing guidelines for siting deposition monitoring stations. In regards to the latter, the Quality Assurance Manager was selected to chair an ASTM working committee (D.22.06.05) charged with developing standards for siting and sampling of atmospheric deposition. The first draft of this standard guide will be discussed at the ASTM D22.06 Atlanta, GA meeting in the fall of 1988.

Section 9 contains a selected discussion paper presented at the last UDDBC meeting. Inclusion of this document in this interim report is solely to demonstrate the type and level of discussion at UDDBC meetings. The discussion paper reflects the views of the author and not necessarily those of the committee.

Workshop on Ecological Quality Assurance In March of 1988 the Quality Assurance Manager was invited to speak at the sponsored by EPA in Denver, CO. The workshop was designed to exchange information about quality assurance programs within organizations involved in ecological research by discussing each groups quality assurance activities, their innovations and their difficulties. Proceedings of the Workshop are available through the U.S. EPA sponsored Forest Response Program, headquartered in Corvallis, OR.

Troubleshooting the Weaknesses and Future Needs of The NADP/NTN Monitoring Network

Precision and Bias Estimates

A proposal for establishing NADP/NTN network precision and accuracy was developed and submitted for funding in September 1987. The proposal outlined a duplicate sampling program to determine the precision and accuracy of NADP/NTN weekly data, seasonal summaries and regional estimates of deposition based upon monitoring network data. Estimates of precisions were to come from a proposed within network co-located sampling program. Bias and accuracy were to be estimated using data from existing between network co-located sampling programs and the proposed co-located sampling program. The proposal was accepted but not funded. Unfortunately this leaves the network without the means to establish the precision and accuracy estimates called for in the NADP Quality Assurance Plan. Data from which estimates of precision can be made are available at only two locations and for limited time periods. One location in North Carolina produced data only for one year. The second location, in Wisconsin has only 18 months of data. Neither location can be considered as representative of the entire network and neither can be used for estimates of bias.

In addition to duplicate sampling, the proposal described a second program for determining precision and bias of rain gage measurements. In this second program precision would have been determined by the rain gage's ability to weigh a known amount of sand at two reference points within the instruments working range. The reproducibility of the difference between the known sand bottle weight and that measured by the instrument at the reference points would have been a measure of the precision or random error. The magnitude of the difference would have been a measure of bias or systematic error. The lack of funding of this portion of the proposal leaves the network with no means to establish rain gage performance in the network. Similar rain gage performance tests were discontinued in 1983 due to lack of funding.

Overall seasonal and regional estimates of precision and accuracy of NADP/NTN rain and chemistry data will have to be inferred from other monitoring network data (e.g. Electric Power Research Institute's daily Operational Evaluation Network, National Weather Service's climate center, etc) or be computed piece-meal from the volume of agency information specific to each network related study. The quality and completeness of this latter approach has never been assessed. Even if this latter approach were successful, it is anticipated that much of the error estimates used in computing overall error estimates will have to come from 'related studies'.

Addition of a Second Laboratory to the NADP/NTN monitoring program

One of the more time consuming tasks of the past contract period has been the addition of a second laboratory to the NADP/NTN monitoring program. Because of contracting requirements, site liaison and the chemical analysis of samples from 18 NADP/NTN monitoring sites administered by the National Park Service were performed by a second laboratory from March 24 through September 29, 1987. During this time period, the Quality Assurance Manager was required to provide additional SOP and QA documentation to the second laboratory as well as coordinate the start up of internal and external quality assurance programs that would eventually allow the evaluation of the second laboratory's data in relation to the data from the original laboratory. At the request of the National Park Service, two audits of the new laboratory were conducted, one prior to the start of operations and one approximately four months into the contract. Completed data and some documentation became available in the early summer of 1988.

A number of inconsistencies with previous NADP practices have prevented a full evaluation of the data. Work is currently scheduled, subject to funding, for the fall of 1988 to re-evaluate field data in a manner consistent with prior NADP/NTN practice. Chemistry data will require more documentation before an evaluation of comparability can be initiated. Audit reports are available through the National Park Services' Acid Rain Coordinator in Washington D.C..

Briefly, no serious deficiencies were found in the laboratory's operations. Many of the 'problems' noted in the audit were associated with data management and site liaison activities. Most were correctable. Some of the noted deficiencies might have been more easily correctable if better documentation of NADP/NTN standard operating procedures in these areas was available. The quality of chemistry results simply lacked documentation. This does not necessarily indicate a lack of quality, only that quality is undefined.

Centralized Documentation and Quality Assurance Reporting

Efforts to expand the NADP/NTN data base to include quality assurance information continue. U.S. Geological Survey Blind-Audit program data and preliminary laboratory quality coding have being worked into the current data base structure. Transfer protocols are being improved. Data from the EPA sponsored Site Visitation Program and the USGS sponsored Intersite Comparison Program are under review in preparation for 1984-1985 Quality Assurance reports.

The Quality Assurance Manager has also been involved in the updating of computer equipment used by the Data Management group at the NADP/NTN Coordination Office. Because of the rapid growth in the amount and variety of NADP/NTN data processed by the NADP/NTN Coordination Office, computer applications have been moved and expanded from a single VAX 11-730 computer to a series of SUN workstations and file servers. Both planning and quality assurance testing was and is being conducted by the Quality Assurance Manager to ensure that the integrity of Network data is maintained.

The Quality Assurance Manager's Office continues to serve as a repository for NADP/NTN Monitoring Network Documentation. Both internal and external quality assurance information is received and evaluated as a part of the Network's documentation. A 1984-1985 quality assurance report on laboratory operations was published by the network during this past contract period (See Section 10) and a 1986 report of laboratory operations is currently under review. Other new titles noted include:

Brooks, M.H., Schroder, L.J. and Willoughby, T.C.. 1988. *Results of External Quality Assurance Program For The National Atmospheric Deposition Program and National Trends Network During 1985.* Water-Resources Investigations Report 87-4219, U.S. Geological Survey, Lakewood, CO.

Brooks, M.H., Schroder, L.J. and Willoughby, T.C.. 1987. *Interlaboratory Comparability, Bias, And Precision For Four Laboratories Measuring Analytes In Wet Deposition, October 1983-December 1984.* Water-Resources Investigations Report 87-4067, U.S. Geological Survey, Lakewood, CO.

Brooks, M.H., Schroder, L.J. and Willoughby, T.C.. 1987. *Bias And Precision Of Selected Analytes Reported By The National Atmospheric Deposition Program And National Trends Network, 1984.* Water-Resources Investigations Report 87-4050, U.S. Geological Survey, Lakewood, CO.

Eaton, W.C. and Tew, E.L., Moore, C.E. and Ward, D.A. 1987. *Summary Report For The National Atmospheric Deposition Program/ National Trends Network (NADP/NTN) Site Visitation Program, For The Period December 1984 through September 1986.* Research Triangle Institute, Prepared For U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Research Triangle Park, NC. August 1987. p.144

Lockard, J.M., 1987. *Quality Assurance Report: NADP/NTN Deposition Monitoring, Laboratory Operations, Central Analytical Laboratory, 1978 through 1983.* National Atmospheric Deposition Program. Natural Resource Ecology Laboratory, Colorado State University, Ft. Collins, CO. May 1987.

Lockard, J.M., 1988. *Quality Assurance Report: NADP/NTN Deposition Monitoring, Laboratory Operations, Central Analytical Laboratory, 1984 through 1985.* National Atmospheric Deposition Program. Natural Resource Ecology Laboratory, Colorado State University, Ft. Collins, CO. May 1988. p. 149.

See, R.B., Schroder, L.J. and Willoughby, T.C.. 1988. *External Quality Assurance Results For The National Atmospheric Deposition Program and National Trends Network During 1986.* Water-Resources Investigations Report 88-4007, U.S. Geological Survey, Lakewood, CO.

A more complete list of NADP/NTN quality assurance related publications appears in Section 11.

SECTION 3
RECOMMENDATIONS

The Quality Assurance Manager's role in the various NADP committees and in scientific organizations involved in deposition research has enabled him to obtain and reconstruct the quality assurance record of the network and maintain a liaison with those responsible for producing the bulk of this information. Furthermore, the scientific setting has allowed the QA Manager to be come a cooperator and coordinator rather than an antagonist -the traditional role of quality assurance officers. The continued participation in these efforts along with a reasonable number of system audits is important if the decentralized documentation of network quality continues.

- The Quality Assurance Manager's participation in auditing, document reviews and scientific meetings should continue to be supported. These are the windows through which the QA Manager can view the network operations.

Now that there is a coordinated effort to gather and archive Network documents the evaluation of data quality is becoming less difficult. The quality assurance reports and other selected agency publications are beginning to document data quality and present it to the scientific community in a more usable manner. The integration of external quality assurance data into the main NADP/NTN data system is beginning to allow this data to be published simultaneously along-side monitoring data.

- Standard formats and transfer protocols for external quality assurance data needs to be established to eliminate redundant data entry and to enable the timely transfer of quality assurance data from the agencies to the NADP/NTN Coordination Office.
- The Quality Assurance Manager should continue to evaluate and document network data quality and network procedures through the publication of integrated quality assurance reports. These reports should be inclusive of all years of operation through current time.

Unlike agency publications, which typically document the quality assurance activities of a single agency or program, integrated reports increase the likelihood that data quality estimates will be appropriate to data use. Studies like the field versus laboratory pH evaluation should be increased to further document the limitations and strengths of the NADP/NTN data set.

One three-quarter time position, however, is not adequate to maintain working relationships with the five primary agencies, two programs (NADP and NAPAP) and numerous committees involved in network quality assurance activities, and, still respond to quality assurance identified deficiencies, organize and evaluate each of the network's quality assurance programs and data, and, produce integrated introspective quality assurance reports and recommendations.

- Staffing levels should be increased to allow for a full-time Quality Assurance Manager and full-time quality assurance technician. This should help increase the frequency of integrated quality assurance reports and allow for continuity in the tracking of network quality assurance activities. The current three-quarter time staffing level provides only enough resources to manage the NADP/NTN quality assurance program on a topical basis.

The regional representativeness of NADP/NTN sites will only be established through the long-term use of the data. The issue of representativeness is specific to each data use.

The network can improve its data users chances for establishing representativeness by continuing to support the stratification and classification of network sites into regionally meaningful groupings or by providing data which will allow such grouping.

- The network should continue to organize and gather information which profiles each of its monitoring stations. This information should be maintained and organized in such a way as to facilitate the selection of sites for regional and topical data analysis.

Co-located station comparisons between NADP/NTN and other networks as well as between side-by-side equipment within the NADP/NTN network are woefully lacking. NADP/NTN has become the reference for deposition monitoring in North America, yet estimates of seasonal and regional precision and bias can only be inferred from other monitoring network data and documents.

- A quality assurance program specifically designed to estimate network precision and bias should be developed and implemented as soon as possible. Emphasis should be placed on comparisons within NADP/NTN and between peer network *data* rather than between the networks' protocols (e.g. daily vs weekly sampling, laboratory A vs laboratory B, etc.)
- The comparability of NADP/NTN data to that of other major networks operating in North America should be established.

SECTION 4
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SECTION 5

NADP/NTN REMEDIAL ACTION PLAN

This plan describes the sequence of actions taken to resolve problems of non-compliance with NADP procedures, protocols and criteria. The plan applies to violations of sampling protocols or siting criteria by established sites; unacceptable performance in field measurements; unacceptable laboratory and/or data management procedures; and failure to participate in Quality Assurance (QA) Programs.

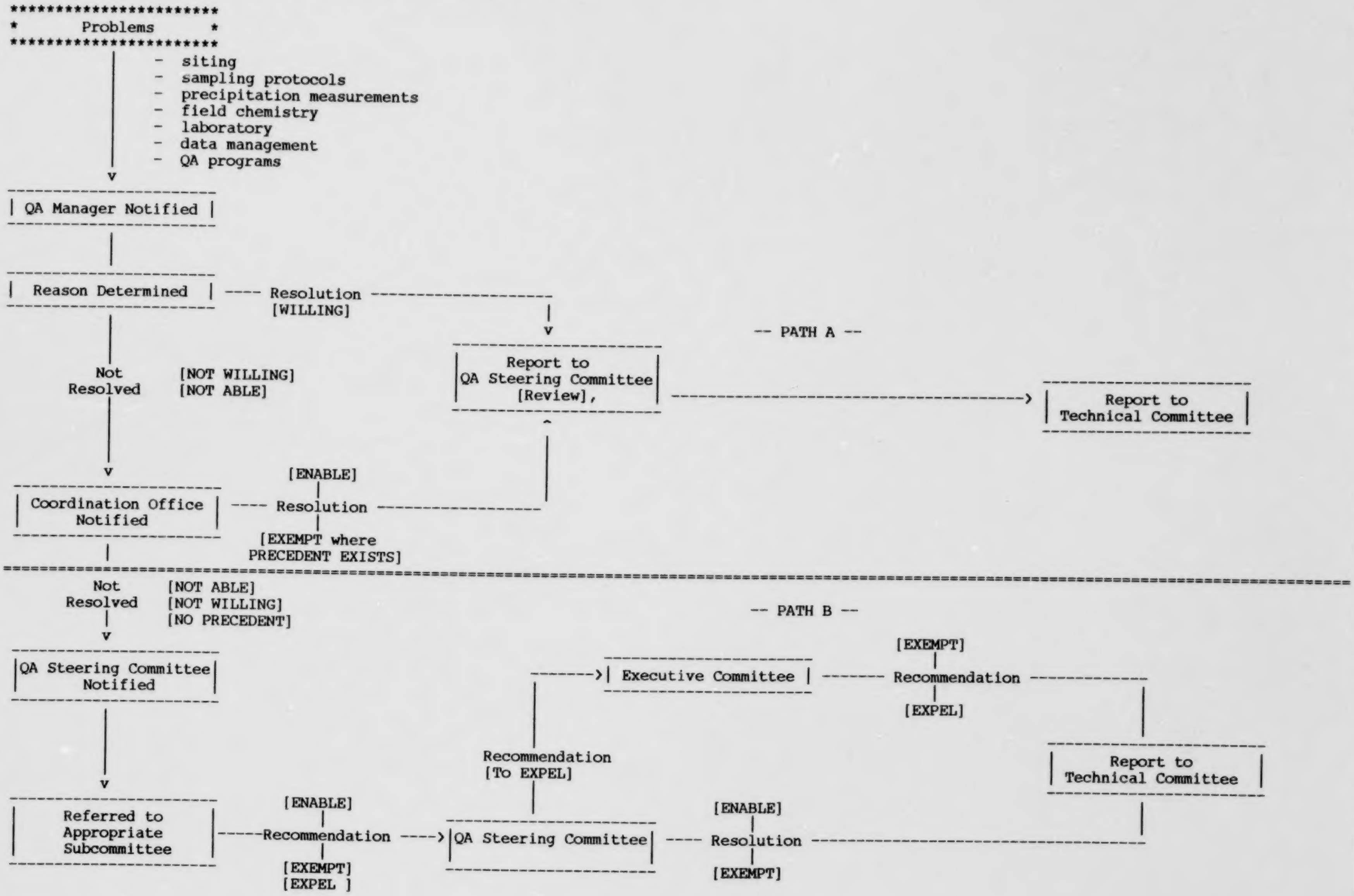
Reports of non-compliance with program procedures, criteria or protocols are initially referred to the **QA Manager** (Figure 1). Possible sources of such reports are the Central Analytical Laboratory (CAL), the USGS Blind Audit Program, the NADP/NTN Site Audits, the Data Managers, the Coordination Office, the NADP Subcommittees, or site operators or supervisors. The QA Manager determines the cause of the non-compliance and, if possible, rectifies the situation by assisting the non-complying party in solving the problem that led to the violation. Problems resolved in this manner are likely to be minor, such as those involving miscommunication between program participants. The problems and their resolution will be summarized in semi-annual reports to the QA Steering Committee.

Problems that cannot be resolved by the QA Manager are referred to the **Coordination Office**. The Coordination Office will work closely with the non-complying party in an effort to achieve compliance. Problems resolved by the Coordination Office in this manner will be reported to the QA Steering Committee on an annual basis. In cases where compliance with program procedures, criteria or protocols cannot be achieved, **and a clear precedent exists** for granting an exemption, the Coordination Office may grant such an exemption. All actions by the Coordination Office and the QA Manager are subject to review by the **QA Steering Committee**. These actions will be reported to the **Technical Committee** in an annual summary report by the QA Steering Committee, and will be documented in the site files or lab files (Figure 1, Path A). The resolution of problems involving site operations will be reported to the Site Supervisor as well, either by the QA Manager or by the Coordination Office.

Situations that cannot be resolved by assisting the non-complying party in conforming to the procedures, criteria or protocols, or where a clear precedent for action on the part of the Coordination Office is lacking, will be referred to the **QA Steering Committee** (Figure 1, Path B), which will refer the problems to the appropriate **Subcommittee(s)**. The Coordination Office will provide as much information as possible to aid the Subcommittee(s) in its analysis of the problem, and may also recommend a course of action. The Subcommittee(s) will review the problem and recommend a course of action to the **QA Steering Committee**. It is the responsibility of the QA Steering Committee to evaluate the recommendations submitted by the

Subcommittee(s) and follow one of two courses of action. If **suspension** from the program is recommended and the QA Steering Committee concurs, the QA Steering Committee endorses the recommendation to the **Executive Committee**. The Executive Committee then evaluates the recommendation, and recommends a course of action to the **Technical Committee**. If an unprecedented **exemption** from protocols or criteria is recommended, the **QA Steering Committee** acts upon the recommendation and simply reports to the **Technical Committee**. Actions by the QA Steering Committee and the Technical Committee are documented in the site and lab files and reported to the Site Supervisor or Laboratory Director. If the Subcommittees and/or QA Steering Committee are unable to reach an agreement on an issue, the issue is referred to the Technical Committee unless suspension is involved, in which case the issue is first referred to the Executive Committee.

Figure 1. NADP/NTN REMEDIAL ACTION PLAN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- sampling protocols
- precipitation measurements
- field chemistry
- laboratory
- data management
- QA programs
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QA Steering Committee
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Resolution
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SECTION 6

Regional Influences on Siting And Sampling in the National Atmospheric Deposition Program/ National Trends Network Monitoring Program

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Abstract

The protocols established by the National Atmospheric Deposition Program that are now in place in the National Atmospheric Deposition Program/ National Trends Network (NADP/NTN) Monitoring Program were developed out of a need to produce a well defined, uniform set of information that would allow the general scientific community to characterize and study atmospheric deposition and its effects on biological systems. Historical data sets had offered only snap-shots of deposition patterns and characterized only selected areas of the United States. Furthermore, results from these previous studies did not include adequate documentation or provide the necessary continuity when the data was applied to long-term research goals.

The NADP/NTN Monitoring program has begun to overcome some of the short-comings of past research efforts. However, its uniform approach to siting, sampling and quality assurance may be creating new problems for future data users. The wide geographic area over which the network operates presents some unique regional problems when a standardized approach to siting and sampling of precipitation and atmospheric chemistry is used. The difficulty of applying a standardized approach to network siting and sampling is examined in the NADP/NTN Monitoring Program. Violations of siting criteria and collector performance statistics are presented as a regional phenomena rather than as a network deficiency. Temporal as well as spatial differences are noted and their effect on data management and quality assurance practices are discussed.

Introduction

The National Atmospheric Deposition Program/ National Trends Network (NADP/NTN) Monitoring Program uses cooperating local, state and federal agencies as well as private industry to operate a network of sites according to a single set of protocols. Each site submits weekly samples to a single central laboratory where chemical analyses are performed. The data from the Network are archived and made available to the scientific community and program participants. The network is unique in its structure and mode of operation in the United States because it represents hundreds of interested individuals and many agencies who cooperate voluntarily to operate deposition monitoring sites and to pool data and research efforts under the NADP umbrella. Because of this cooperation, the network's standardized procedures for the collection and evaluation of wet deposition are recognized throughout North America.

The protocols that are now in place were developed out of a need for a well defined, uniform set of information that would allow the general scientific community to characterize and study atmospheric deposition and its effects on biological systems (NADP, 1978). Historical data sets offered only brief pictures of deposition patterns and characterized only selected areas of the country. Furthermore, results from these studies did not provide adequate documentation or the necessary continuity to apply the data to long-term research goals (Interagency Task Force On Acid Precipitation, 1982; Likens, 1976; Pack and Shepherd, 1983).

The NADP/NTN Monitoring program has begun to overcome some of the short-comings of past research efforts. However, its uniform approach to siting, sampling and quality assurance may be creating new problems for future data users. Solutions to these problems will depend upon the users understanding of the network's data collection techniques and his consideration and use of the variety of information that the network makes available. Among those considerations should be the unique regional differences in network quality that result when a standardized approach to siting or sampling is implemented over such a large geographic area. These regional differences can occur when; siting requirements are easily met in one region, but, virtually impossible to achieve in another; when the standard collector, designed for temperate areas, operates outside of its design limits in some areas; or, when data managers, rather than data users, are unintentionally placed in the position of determining the validity of non-conforming data.

Siting Requirements

NADP/NTN monitoring sites are generally selected to represent major physiographic, agricultural, aquatic and forested areas within each cooperator's state or region. Wherever possible, collection sites include locations where aquatic, terrestrial, atmospheric, or other deposition related research is already underway. Because the monitoring stations are meant to serve many scientific disciplines and address a variety of atmospheric deposition concerns, siting criteria have been established to describe the sites in a unique way. (Siting criteria are given in Appendix A). Location and emission information are gathered in a manner which allows the sites to be characterized at three concentric distance intervals. The information for each interval assumes that sources located outside of the cut-off distances become part of the regional make up of the area. Within the interval, mentioned sources *may* be a significant source of bias in assuming regional representativeness. The distance intervals are; within 30 meters, which is considered the immediate site itself, 30 meters to 1 kilometer, which is designated as the area of local influence, and, 1 kilometer to 50 kilometers, which is assumed to be the area of regional influence. Potential sources beyond 50 kilometers are not routinely described. A summary of critical distances for primary sources of interest to the NADP/NTN monitoring program is given in Table 1 while a more detailed explanation appears in Appendix_A (Bigelow, 1984).

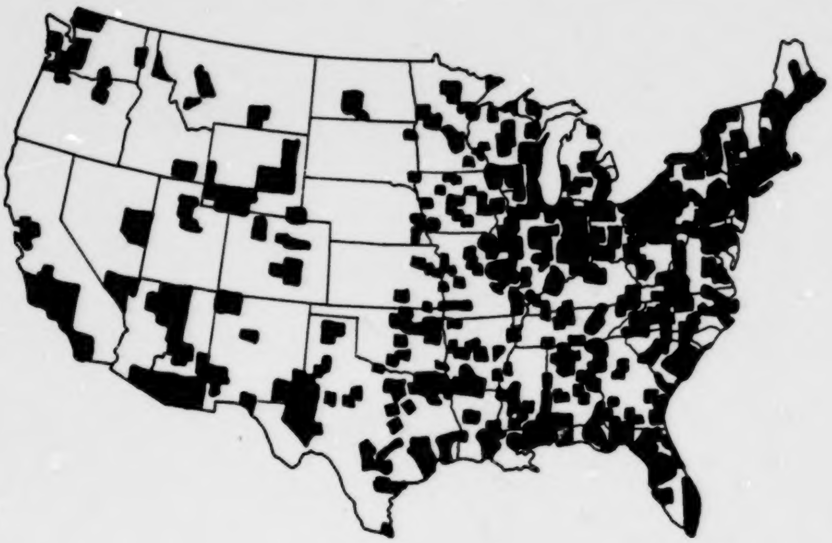
Noteworthy is the fact that the criteria do not explicitly forbid siting below the critical distances. Rather these distances are considered goals. Generally the NADP/NTN monitors in what would be considered 'background' areas. However, if a region is characterized by a particular type of source, regional stations that fail to meet requirements for that type of source are not excluded from network consideration.

Table 1. Critical Distances for Siting NADP/NTN Monitoring Stations

Potential Sources	Distance From The Collector Minimum		Background
Heavy Industry	10 km	(20 if upwind)	50 km
Suburban/Urban Areas	10 km	(20 if upwind)	50 km
Populations > 75,0000	20 km	(40 if upwind)	50 km
Moving Sources	100 m		10 km
Feedlots/Dairies, etc	500 m		1 km
Grazing Animals	20 m		1 km
Surface Storage	100 m		1 km
Parking Lots	100 m		200 m
Rain Gage	5 m		30 m

In western regions of the United States, where urbanization and industrialization tends to be sparse or clustered, criteria concerned with point and areas source emissions are, in general, easily met. In the eastern and mid-western regions, however, population and industrial development are much more extensive and siting becomes more difficult (See Figure 1).

Figure 1 Sulfur Dioxide Emissions Density (> 3 tons/mile, 1980)
[from U.S. Congress, Office of Technology Assessment, 1984]



For Network designers, data managers and data users these standard requirements pose a dilemma. How closely must the criteria be met to ensure 'high quality' data? If they must be followed closely, how does one monitor background deposition in an industrialized region? Should these areas be excluded from the monitoring effort? How should background data be estimated (for isoplething or modelling, for instance) if no monitoring stations are available? If they are available, how should they be interpreted as compared to 'true' background sites?

The extent of the siting problem and its effect on data interpretation are demonstrated in Table 2. The Table groups network siting violations regionally by ecoregion [7] and presents three different interpretations of the siting violations at NADP/NTN stations operating in 1983.

The first interpretation (column 4) is based upon site visits, emission inventory tabulations and reviews of NADP/NTN Site Description Questionnaires conducted by network designers (Bigelow, 1984, 1986; Robertson and Wilson, 1985). The second interpretation is based upon point source emission information recently made available through the National Acid Precipitation Assessment Program (NAPAP) (T. Clark, personal communication) [8] as well as the NADP/NTN Site Description Questionnaires used in the first interpretation. It strictly applies the siting criteria to each site and ignores any first-hand information provided by site auditors. The third interpretation uses criteria developed for use in modelling by the Unified Deposition Data Base Committee (Lusis et al., 1986a, 1986b; UDDBC, 1986). In this interpretation sites are 'graded' according to a sliding scale. The 'most useful' sites have no identified siting problems, while the least useful sites have the most identified siting problems. For modelling purposes some sites are identified as 'not usable'. To qualify for the 'most useful' status, sites must have been declared 'regionally representative' by their Network managers (i.e. passed Network criteria) and have no more than 10,000 tons/ year of either SOx or NOx within 50 kilometers of their location. Emission information comes from the same source used in the second interpretation.

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[7] The Ecoregion is a regional discriminator developed by Bailey (Bailey, 1978 and 1980, Bailey and Cushwa 1981) that combines biotic and abiotic factors such as topography, vegetation, climate (i.e. rainfall, temperature) and geology into one classification system.

[8] The NAPAP 4.0 Emission Inventory is available through the United States Environmental Protection Agency

Table 2 Three Interpretations of Regional NADP/NTN Siting Criteria Violations

Ecoregion Domains	Approximate Location	No. of Sites	Sites Failing Regional Siting Criteria From Visits	 Strict Interpretation	 UDDBC
2300	South and Piedmont	23	24%	76%	82%
2400	Pacific Northwest	7	0%	43%	0%
2200	Midwest (industrialized) and Northeast (high pop.)	21	24%	38%	81%
2500	Prairies	12	25%	33%	50%
2100	Great Lakes Northeast (low pop.)	25	8%	28%	32%
2600	California	4	50%	25%	50%
3000	Great Plains Mountains Great Basin	22	5%	14%	27%

The strict interpretation of the siting criteria (center column) and its application to data analyses would exclude 76% of the sites in the Southern and Piedmont portions of the United States. Eighty-two percent would be excluded from the UDDBC interpretation (an actual difference of only one site). Each of these interpretations excludes sites from data analyses even though they may be typical of their regions. The Great Plains, Mountains and Great Basin areas of the country generally have the fewest violations, primarily due to their lower densities of population and industry. However, violations will occur if monitoring is required near one of the industrialized areas such as the eastern slope of the central Rocky Mountains.

The figures associated with the Pacific Northwest best describe and summarize the task of the data user and the problems encountered when applying standard siting criteria to a data analysis. In the strict interpretation (fifth column) almost half of the sites in the region are removed from analyses because there is at least one source present within 10 kilometers of each of the excluded monitoring stations. However, if the amount of emissions is taken into account, as was done by the UDDBC- the sources become inconsequential (column six). In fact, this is the conclusion that the West Point group came to based upon their visits to the area (column 4).

Which interpretation should be used? Which is the least controversial? Which is the safest interpretation? The fact that there were, or, were not sources within the 10 kilometer cut-off criterion serves as a basis for data users to decide if, for their own interpretation of the data, the information presented is valid and usable for their application. Additional information, such as emission rates, may be required. The criterion, however, has alerted users to some of the site's or region's limitations.

The regional emission 'problem' is not unlike the problem of including or excluding information from areas of dissimilar topography or from areas demonstrating strong coastal influences. Valid reasons can be found and guidelines can be developed for including or excluding data from these regions into one data interpretation (i.e. sea salt corrections). One must first be alerted to the disparities however, before the guidelines can be developed and implemented.

Another use of standardized siting criteria is as a reference in assessing the impact of unpredictable or unmeasured variables at monitoring stations. Take for example, the second NADP/NTN siting criterion listed in Appendix A. *The collector should be oriented with the WET side bucket to the west and the sensor pointing north.* Many researchers siting similar equipment would recommend siting the collector into the prevailing wind. Although this might seem desirable in all circumstances, it is of no consequence in a forest clearing or other highly sheltered area where wind speeds are negligible. In addition it should be recognized that in a great majority of areas the prevailing winds are not known or are seasonal in nature. The purpose of the standard in this instance is to provide a uniform, documented reference orientation. In forest clearings the criterion is probably best ignored. In windy areas more information would be needed to determine the effect, if any, of orientations that put the WET bucket away from the wind.

The NADP/NTN Monitoring Program has established a standardized set of siting criteria to be used by all sites in the Network. It's greatest utility, however, is not as an absolute approval or declaration of a station's regional representativeness, but, rather as a standardized body of information which can be used to evaluate the appropriateness of the site's atmospheric deposition data for a particular analysis.

Collector Performance

The NADP/NTN Monitoring Network utilizes a Belfort 5-780, Universal, 0-12 inch, dual traverse, weighing, recording rain gage (Belfort Instrument Co.) and an Aerochem Metrics Model 201 or 301 Wet/ Dry Precipitation Collector (Aerochem Metrics, Inc.) to quantify and capture wet deposition at each of it's more than 200 monitoring sites. The Belfort rain gage is used to measure the amount of precipitation while the Aerochem Metrics collector is used to capture wet deposition for further chemical analysis. The Belfort rain gage is a passive, opened topped, can type of rain collector with a 324.29 cm^2 orifice. The gage stands approximately 100 cm above ground level. It measures precipitation by weighing the volume of liquid that enters the orifice. As liquid accumulates in the gage, a weighing mechanism displaces a lever mounted nib which records the displacement on a pre-printed calibrated chart. The Aerochem Metrics collector is a modified HASL (Volchock and Graveson, 1976) deposition collector that utilizes a 3½ gallon pail, a rain sensor and a mechanical lid assembly to capture wet deposition and exclude dry deposition. A foam seal on the underside of the lid maintains a semi-gas tight seal on the bucket to prevent the captured liquid from coming in contact with dryfall. The bucket has an opening of 678.87 cm^2 and sits approximately 145 cm above ground level.

Siting requirements in the NADP/NTN network specify that the Aerochem Metrics collector is to be no more than 30 meters and no closer than 5 meters to the Belfort rain gage. It also specifies that both the collector and rain gage should be free from overhead obstructions. A distance equal to the height of any object should be maintained between that object and either instrument. Modifications or the addition of options to either instrument is expressly discouraged, although Alter shields have been approved for use in certain areas identified as susceptible to sustained winds. Because the measurements are made in close proximity to each other, the two measuring devices, under ideal conditions, should agree with one another if they are measuring the same precipitation. Typically they are within 5 percent of each other with the Aerochem Metrics collector measuring the lower of the two values. On a weekly basis the network considers ± 15% to be acceptable. However, this criterion does not acknowledge that the performance of the Aerochem collector exhibits some regional and seasonal characteristics which can potentially impact data interpretations.

Figure 2 presents the annual average weekly catch efficiency (bucket volumes ÷ rain gage volumes) for data collected in 1984 and 1985. On an annual basis a spatial bias is apparent. The bias is caused by the higher frequency of wind, snow and to some degree small volume precipitation events that typify this part of the country (Great Plains and Rocky Mountains). Figure 3 displays the same data as in Figure 2 but only that portion collected in the winter (December, January and February) months. Comparing Figure 2 to Figure 3 illustrates that the collector performance phenomena is also seasonal. In the Great Plains and mountainous regions, the performance of the collector deteriorates in the winter. Catch efficiencies drop from approximately 70% to below 50%.

Figure 2 1984-1985 Annual Average Weekly Catch Efficiencies

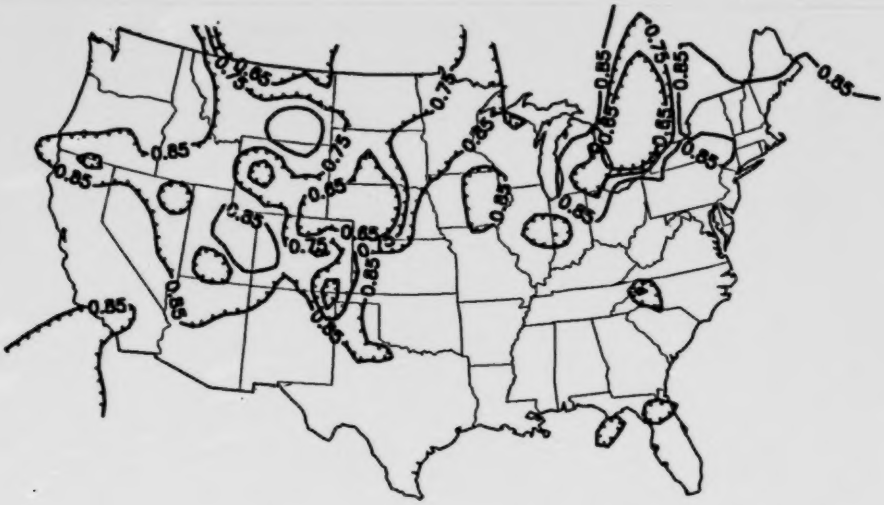
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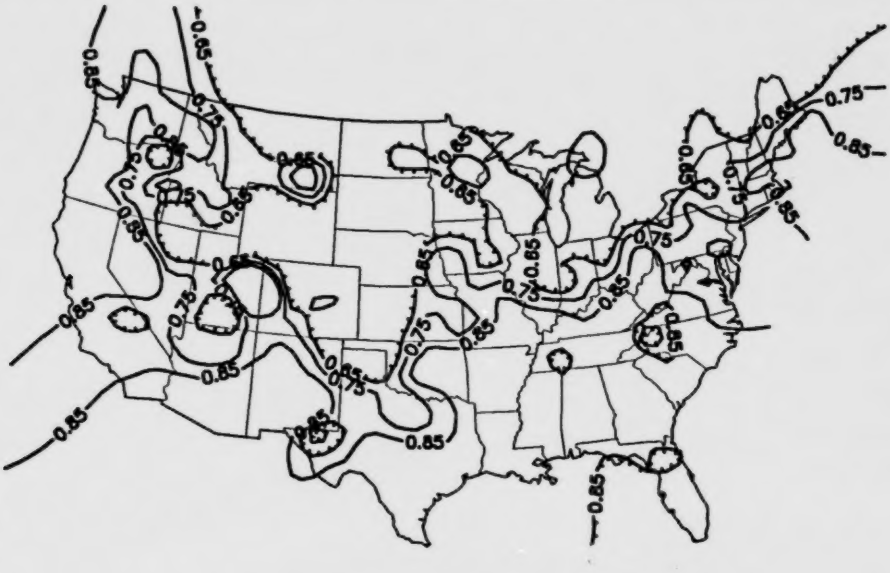
Figure 3 1984-1985 Average Winter Weekly Catch Efficiencies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In the Northeast portions of the country where wind is generally not a problem, freezing rain and heavier wet snows prevent the electronic components from performing optimally. The mechanical lid moves more slowly, the heater works longer and the clutch slips more, ultimately resulting in collector breakdown. This region of the country experiences twice the network average in collector component failures (Bigelow, 1986).

Haasz (1979) has demonstrated that the bucket design (opening and depth) contributes to lower catch by allowing captured snow to be reentrained and removed from the bucket during periods of high winds. Wind also alters the angle and velocity of snow (and some rain) reaching the bucket thereby reducing catch. The sensitivity of the sensor, approximately 75 ohms, and its ability to melt snow also contributes to lower catch when the moisture content of the snow is low or ambient temperatures drop. In spite of these deficiencies this style of collector is recognized as the most appropriate for large distributed monitoring networks (Galloway and Likens, 1976, Topol et al., 1984). It should also be noted that all collectors that utilize similar configurations of bucket and sensor designs, and motor box and lid seal construction are, most probably, operating outside of their design limits under these conditions. Because acid deposition was previously considered to be a phenomena of more urbanized portions of the country, and since annual precipitation in the affected areas is generally low, monitoring was not routinely conducted in these areas. Prior to the initiation of routine monitoring in the mountains and Great Plains, the deficiencies in collector performance were considered insignificant in the context of the total monitoring effort. It is now recognized that in certain parts of the country these deficiencies can raise serious questions as to the representativeness of the captured precipitation.

The NADP/NTN Monitoring Program calculates and reports collector catch efficiency for each sample collected in the network. In addition to this week by week quality assurance calculation, collector catch efficiency is computed seasonally and annually as a percent of the *total* volume detected by the rain gage over the time period being summarized. This calculation allows the data user to evaluate the issue of the representativeness of the volume of rain sent for analysis on a seasonal (annual) basis as well as the performance of the collector week by week during the season. In the winter months, on a volume basis, catch efficiencies do not drop significantly in the Northeast or eastern Great Lakes region as they do in the Great Plains and Rocky Mountains. This indicates that the *volume* of rain missed by the collector is not an appreciable amount compared with the total precipitation. A bias in the *type* of precipitation sampled, such as is indicated by the seasonal bias, may impact annual deposition determinations.

Data Management And Quality Assurance

The NADP/NTN Monitoring Program utilizes a hierarchical method of data management and quality assurance which involves passing information from participating monitoring sites to a central analytical laboratory and on to a coordinating and management group. Audit information and external quality assurance results produced outside this pathway finds its way to the coordination group in a similar fashion, except instead of passing through a central laboratory, the information passes through the agency responsible for completing the auditing task. Each group is responsible for gathering and evaluating the information and providing the results *and their evaluation of the results, along with supporting information,* to the coordinating group. The program philosophy is to screen and codify data as it moves on to the coordinating group without sequestering or removing supporting information during the numerous data transfers. Coded or 'flagged' data alert the subsequent data management groups and ultimately the user, of a *potential* bias or deficiency. Some data may be passed in summarized form, however, the supporting information and documentation must clearly indicate the appropriateness of the summary. One of the common summary examples occurs when the laboratory passes along only one value for a chemical determination on a single sample, even though replication was performed. The supporting documentation contains the statistical evaluation of the replicates that have been performed on the sample set. The data user then has available not only the chemistry value, but also a quality assessment of the value.

The data flags and quality assessments provide additional information upon which data interpretations can be based. However, by providing this information, the program is transferring much more responsibility for data quality to the data user. Additionally the user is presented with the formidable task of understanding and evaluating the data decisions that will define the NADP/NTN monitoring data set.

Because of the Network's goal of providing a long-term, robust data set that will be usable for a number of scientific disciplines, the NADP/NTN has separated the interpretation of the data from the monitoring effort. However, the program has recognized that for this to be successful, more information about data quality will have to be documented. As was pointed out in the previous sections, the failure of a site to meet a siting requirement or the failure of a collector to perform optimally may not be sufficient enough reason to remove the information from a data user's consideration. This is especially true if the deficiencies can be documented and perhaps made more quantified -even at a later date.

Managers and technicians who have responsibility for transferring data are often not data users, yet, they are often charged with applying the established criteria or standards of quality to the information being gathered. The tendency is to remove or identify and then sequester 'bad' values from the data set to afford the data user the 'best' quality data. This encourages the data managers to make decisions about the data that might more appropriately be made by the user.

As an example, each NADP/NTN site's data is subjected to an ion balance quality assurance check (Stensland and Bowersox, 1985). Samples whose cations do not equal anions within certain established limits had been considered to be the result of analysis errors in one or more of the chemical determinations. The general consensus at the beginning of the program was that these values should be removed from the data set. Instead the program noted the imbalance and reported the data. Subsequent evaluations by Stensland and Bowersox (1985) and Lockard (1985) revealed that the imbalances where most probably due to an unmeasured ion and that the imbalance was typically characteristic of the measured chemical constituents at each site. Had the program 'removed' these samples from the data set, the phenomena might not have been discovered and approximately 6.5% of the samples would have been unavailable to data users. At some sites the percentage of unavailable information might have been even higher. This is an example of data managers assuming an interpretive role in assessing data quality. It prevents the data user from obtaining information which would allow him to make his own quality judgement.

The NADP/NTN program recognizes that the interpretation of its data set may change as new discoveries are made and new interpretive techniques are developed. Because of this recognition, the Network is attempting to gather and present enough information to ensure that the data will be useful long after the project is complete and to ensure that the information gathered will be adequate enough for subsequent interpretations. To accomplish this the network is carrying forward an additional body of information that documents the quality of the data and the evaluations of data quality.

Summary

The NADP/NTN Monitoring Program is a unique attempt at providing a broad based scientific community with some basic data upon which atmospheric deposition and its effects can be characterized and studied. It recognizes that regional differences in atmospheric phenomena make it difficult to apply standards over such a large geographic area. Rather than trim its data set by some standard technique the network has chosen to provide additional quality assessment information to the data user and encourage him to evaluate the quality of the data in the full context of its use. The main disadvantage for the user is that it requires him to become much more knowledgeable about the data set he is using.

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APPENDIX A : NADP/NTN Siting Criteria

ON SITE On Site Requirements (within 30 meters)

1. Recommended Installation of the collector is on the standard 3 foot high aluminum base over undisturbed ground. In areas having an accumulation of over 2 feet of snow per year, the collector may be raised off the ground on a platform. This platform will be no higher than the maximum anticipated snowpack. In general, platforms are discouraged.
2. The collector should be oriented with the WET side bucket to the west and the sensor pointing north.
3. Naturally vegetated, level areas are preferred, but grassed areas and slopes up to ± 15% will be tolerated. If possible, such ground cover should surround the collector for a distance of approximately 20 meters. The slope should be within the prescribed value in the ground cover area. In farm areas a vegetated buffer strip must surround the collector for at least 20 meters.
4. The base of the collector will not be enclosed.
5. Objects with sufficient mass to deflect the wind (with the exception of an alter wind shields) over 1 meter high will not be located within 5 meters of the collector.
6. The rain gage should be located within 30 meters of the collector, but no closer than 5 meters. It's orifice should be located within 1 foot of the same level as the orifice of the collector.
7. Collectors located in areas which normally receive snow will only have a snow roof installed on the moving lid of the collector when problems with opening and closing are encountered. Such a lid will be left on year round.
8. Annual vegetation will be maintained at less than 2 feet.
9. No object or structure shall project onto the collector or rain gage with an angle greater than 45 degrees from the horizontal (30 degrees is considered optimal, but 45 degrees is the highest angle acceptable). Therefore the distance from the sampler to the object must be at least equal to the height of the object (preferably twice the height of the object). Pay particular attention to anemometer towers and overhead wires.

LOCAL Local Requirements (within 1 km)

10. No surface storage of agricultural products, fuels, vehicles, or other foreign materials within 100 meters of the collector will be allowed. Parking lots and maintenance yards with frequent use are a particular problem.
11. Grazing animals and pasture will not be closer than 20 meters to the collector. Feedlots, dairy barns, etc, in which large concentrations of animals are housed will be no closer than 500 meters to the collector.
12. Frequent moving sources of pollution, such as air, ground, or water traffic or the medium on which they traverse (e.g. runway, taxiway, road, or navigable river) within 100 meters of the collector. The local road net around the site is of particular concern.
13. Residential type buildings should not be within a 30 degree cone.

REGN Regional Requirements (within 50 km)

14. Continuous industrial-type operations such as factories, chemical plants, power plants, etc will not be within 10 km of the collector. Additionally if the emissions sources are located in the general upwind direction (i.e the mean annual west-to-east flow in most cases) of the collector, then they should be no closer than 20 km to the collector.
15. The collector should not be located within 10 km of a moderate-sized suburban or urban area. A general definition of this classification is one having 10,000 or more people. This

distance should be increased to 20 km if the urban area is in the general upwind direction of the collector. For the larger cities (i.e. populations greater than 75,000) the collector should be no closer than 20 km if it is in the upwind direction, and 40 km if it is in the downwind direction.

SECTION 7
Observer Turnover in the NADP/NTN Network: Implications for Training

Carol Simmons
Malcolm Still
Gary Stensland
David Bigelow

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INTRODUCTION

The NADP/NTN Quality Assurance Plan states that field observations are to be made by trained site personnel. Towards this end, the program provides training for up to 56 field personnel a year through a semiannual training course held at the Central Analytical Laboratory (CAL). This course is currently the only mechanism for providing formal training to the field observers at approximately 200 NADP/NTN sites. Although trained personnel are encouraged to provide on-site training to other field observers at their sites, there is no procedure for monitoring on-site training, thus the quality and extent of such training are unknown. Additional forms of informal training include the numerous contacts between Program personnel and the sites, as well as informal training that is incidental to the site audits.

At the request of NADP Subcommittee 1, data from the NADP/NTN field observer report forms were analyzed to estimate the rate of turnover of field observers in the Network and to evaluate the extent to which field procedures have been performed by CAL-trained observers. The results of these analyses are discussed in light of the requirement for trained field observers at the NADP/NTN sites. Alternative methods for supplementing the training provided by CAL are described.

METHODS

The analysis of observer turnover was based on the initials recorded on the field forms that accompany every sample sent to CAL for analysis. This approach has several limitations that should be recognized. First, although the data were screened to eliminate cases where different sets of initials referred to the same individual (due to name changes, observer inconsistencies, difficulties in interpreting the observer's writing, etc.) some such discrepancies probably remained undetected. Second, because the observers were counted on a site-by-site basis, the (few) observers who worked in two sites were counted twice when network-wide statistics were calculated. Finally, it is important to recognize that although there is space for only one set of initials on the form, several individuals may actually participate in the collection and measurement of a single sample. For example, one individual may collect the sample and do the equipment checks, then a second may make the pH and conductance measurements. It is even possible that a third individual, such as the site supervisor, signs the form.

Field form data were analyzed over three different time periods. An analysis of long-term data was done in January 1987. It covered the period from the establishment of the first site through January, 1986; more recent data were not available at the time the analysis was initiated. Analyses of short-term data focused on two 1-year periods: 1 February 1985 through January 1986, and 1 February 1986 through January 1987. Note that the first 1-year period corresponds to the last year of the long-term data.

RESULTS

Long-Term Data

In the period from the inception of the NADP/NTN network through January 1986, 1104 observers recorded their initials on field forms. 217 sites operated at some time during this period; three of them in Canada. The number of observers per site ranged from one (16 sites) to 38 (one site). Because the latter site had twice as many observers as the site with the next largest number, it was excluded from subsequent analyses. The Canadian sites were also excluded. The number of sites was thus reduced to 213 and the observers to 1057.

The frequency distribution of the number of observations per observer is strongly skewed: a large percentage of the observers made only a few observations (Table 1 and Figure 1). Given this asymmetrical distribution, the quartile values (25th, 50th and 75th percentiles) may be more informative than the mean. These values are reported in the summary tables as the first, second and third quartiles, respectively. During the summary period, the mean number of observations per observer was 36.8; however, fully half of the observers made 12 or fewer observations, while 25% made 3 or fewer. During this same period, the mean length of time the sites were in operation was 182.7 weeks (Table 2). Half of the sites had operated 150 weeks or longer.

The number of observations made by an observer is not necessarily indicative of the length of time the observer has participated in site operations. At some sites, individuals trade off responsibility for operating the site. An alternative measure of observer "longevity" is the time elapsed between the first and last (most recent) observations by a given individual. In January 1986, the mean length of time observers had participated in site operations was slightly under two years; the median (50th percentile) was 68 weeks (Table 3). As one would expect, both the mean length of time worked by observers and the number of observers per site tend to increase as sites operate for longer periods (Tables 4 and 5).

However, some sites that have operated many years have had only one or two observers (note the minima in Tables 4 and 5).

In order to have had 90% of the observations made by CAL-trained observers, at least 561 observers would had to have been trained. By January 1986, 185 site personnel had actually been trained at CAL.

Short-Term Data

The results of the analyses of the short-term data were generally similar for the two 1-year time periods; therefore, only the latter period will be discussed. Data from both periods are summarized in Tables 6 through 9. For each time period, the descriptive statistics were based on the sites that operated the entire year (178 sites in 1985 and 190 in 1986).

In the period 1 February 1986-January 1987, 549 observer's initials were recorded at 190 sites (Table 6). The mean number of observations per observer was 18.0, while the 25th and 50th percentiles were 3 and 9 observations, respectively. Thus, over the short-term, as over the long-term, many of the observers made a small number of observations. The number of observers per site ranged from 1 to 10 (Table 7 and Figure 2), with a mean of 2.9 and a median of 3.

Observers were classified as "new" if their initials had not appeared on field forms prior to the summary period. They were considered "trained" if they had attended a CAL training course prior to the end of the summary period. In the period 1 February 1986-January 1987, 131 trained observers (23.9% of all observers) signed 40.3% of the field forms (Table 8). At least one field form was signed by a CAL-trained observer at 115 of the 190 sites. 159 observers (29.0% of all observers) were new to the program. These new observers were responsible for 15.3% of the samples (Table 9). Eight of the new observers were trained at CAL in 1986.

DISCUSSION AND ALTERNATIVES

The large number of initials recorded on field forms indicates that there are many individuals involved in the collection and/or processing of precipitation samples at the NADP/NTN sites. In most sites, two or more individuals regularly participate in the site operations during a single year. Most sites also make use of substitutes. In both 1985 and 1986, the number of new observers exceeded the capacity of the CAL training program by approximately 100; however, in both years the new observers were responsible for only a small percentage (approximately 15%) of the observations in the network. Many of these new observers may not continue to participate in site operations, or may only participate occasionally.

These results indicate the difficulty of obtaining a goal of having all site observations made by CAL-trained observers. Unfortunately there is no information about the extent to which CAL-trained observers have undertaken the training of other observers at their sites, or the quality of such training. In order for the NADP/NTN Network to obtain its objective of having trained observers make field observations, alternative forms of training are needed to supplement the semiannual training course at CAL. In addition, sites should be informed of the importance of training and should be discouraged from using untrained substitutes to operate the site, except as a last resort. Two alternative approaches to supplementing the CAL training program are described below. In addition, some elements of each alternative could be combined to produce other viable alternatives.

Alternative 1

Train one "operator" at CAL who is designated to ensure that his/her site has a sufficient number of site-trained personnel ("observers"). Require each site to have one person thus designated and trained. Formalize on-site training for the other personnel. (Two types of certification might be awarded: one for CAL-trained operators, the other for site-trained observers.) This approach would require:

- Training at CAL for one individual from each site that does not currently have a CAL-trained operator (up to 80 sites)
- Training of 200 site operators to conduct on-site training for other personnel. (For some sites this could be combined with the above)
- Offering periodic refresher courses for CAL-trained operators
- Development of training materials such as films and training guidelines for dissemination to 200 sites
- A verification system for ensuring that all site personnel have had the required training. Documentation in site files.

Some possible variations to the above are: (1) require different levels of training for the various tasks involved in site operations (bucket removal/transport to lab; field measurements/prep for shipment; record keeping), (2) award "operator" certification to those site personnel who have been operating sites for years (but have not attended CAL training) after an acceptable performance on the NADP/NTN site audit, (3) expand and formalize the role of RTI in providing on-site training in conjunction with the site audits. Each variation has positive and negative aspects which should be considered.

Alternative 2

Train an instructor from a participating agency to provide training in a particular region. This would require:

- Cooperation of NADP/NTN participating agencies
- Training for up to 50 part-time "regional instructors"
- Periodic refresher courses for instructors
- A system for verifying and documenting the training of field observers
- Sufficient resources to reimburse instructors and site personnel for increased travel (?)
- Development of training materials such as films and training guidelines for dissemination to 200 sites

Regardless of the course of action chosen, there is a need for a better understanding of the roles of various site personnel in the operation of the individual sites. For example, there is a need to document the extent to which different individuals at each site are involved in the various phases of sample collection and processing.

TABLES AND FIGURES

Table 1. Number of observations per observer for the period July 1978 through January 1986.

Mean	36.8 (observations)	Quartile 1	3
Std. Dev.	62.6	Quartile 2	12
Range	1-377	Quartile 3	41
N	1057 (observers)	Skew	2.99

Table 2. Number of weeks of operation by sites in the NADP/NTN Network, July 1978 through January 1986.

Mean	182.7 (weeks)	Quartile 1	86
Std. Dev.	112.5	Quartile 2	150
Range	8-395	Quartile 3	292
N	213 (sites)	Skew	0.42

Table 3. Time period (weeks) between first and last (most recent) observations by NADP/NTN observers for the period July 1978 through January 1986.

Mean	69.3 (weeks)	Quartile 1	7
Std. Dev.	84.8	Quartile 2	36
Range	1-395	Quartile 3	103
N	1057 (observers)	Skew	1.67

Table 4. Time period (weeks between first and last (most recent) observations by observers at sites in operation for different lengths of time.

Weeks of Operation	Number of Sites	Time Period Between First and Last Observations:						
		Mean	(Std. Dev.)	Minimum	Q1	Q2	Q3	Maximum
1-52	20	20.2	(7.9)	9.0	13.0	20.0	25.4	35.0
53-104	49	41.4	(15.4)	15.9	30.8	39.4	47.6	85.0
105-156	43	71.9	(34.1)	24.0	47.6	59.5	89.2	156.0
157-208	19	91.9	(56.4)	32.2	43.1	78.5	134.4	203.6
209-260	16	98.6	(46.4)	30.9	78.3	91.6	115.6	215.5
261-312	31	100.1	(66.3)	26.4	58.9	83.3	111.9	295.0
313-364	16	176.5	(117.1)	44.5	86.6	141.9	262.2	386.1
365-395	19	138.2	(63.8)	70.2	91.7	118.8	175.2	320.5

Table 5. Number of observers on record per site for sites in operation for different lengths of time.

Weeks of Operation	Number of Sites	Number of Observers on Record per Site:						
		Mean	(Std. Dev.)	Minimum	Q1	Q2	Q3	Maximum
1-52	20	3.2	(1.7)	1	2.00	3.00	4.00	7
53-104	49	3.6	(2.0)	1	2.00	3.00	4.00	11
105-156	43	4.0	(2.6)	1	2.00	3.00	5.00	10
157-208	19	4.7	(2.4)	1	2.00	4.00	7.00	8
209-260	16	5.9	(4.4)	1	3.00	4.50	6.50	18
261-312	31	8.4	(4.7)	1	4.25	9.00	10.75	19
313-364	16	5.9	(5.1)	1	2.00	4.00	9.00	16
365-395	19	5.7	(2.8)	2	3.25	5.00	7.00	11

Table 6. Number of observations per observer at NADP/NTN sites for the periods 1 February 1985 through January 1986, and 1 February 1986 through January 1987.

	Feb. 1985-Jan. 1986	Feb. 1986-Jan. 1987
Mean (observations)	18.6	18.0
Std. Dev.	(18.3)	(18.1)
Range	1-52	1-54
N (Observers)	493	549
Quartile 1	3	3
Quartile 2	10	9
Quartile 3	36	32

Table 7. Number of observers at NADP/NTN sites during the periods 1 February 1985 through January 1986, and 1 February 1986 through January 1987.

	Feb. 1985-Jan. 1986	Feb. 1986-Jan. 1987
Mean (observers/site)	2.8	2.9
Std. Dev.	(1.5)	1.6
Range	1-8	1-10
N (sites)	178	190
Quartile 1	2	2
Quartile 2	2	3
Quartile 3	3	4

Table 8. Number of observations by trained vs. untrained observers.

a. 1 February 1985-January 1986

Observer Category	Number of of Observers	Percent of of Observers	Number of Observations	Percent of Observations
Trained	132	26.8%	3864	43.5%
Untrained	361	73.2%	5011	56.5%
TOTAL	493	100.0%	8875	100.0%

b. 1 February 1986-January 1987

Observer Category	Number of of Observers	Percent of of Observers	Number of Observations	Percent of Observations
Trained	131	23.9%	3927	40.3%
Untrained	418	76.1%	5902	59.7%
TOTAL	549	100.0%	9881	100.0%

Table 9. Number of observations by new vs. returning observers.

a. 1 February 1985-January 1986

Observer Category	Number of Observers	Percent of Observers	Number of Observations	Percent of Observations
New	160	32.5%	1294	14.6%
Returning	333	67.5%	7581	85.4%
TOTAL	493	100.0%	8875	100.0%

b. 1 February 1986-January 1987

Observer Category	Number of Observers	Percent of Observers	Number of Observations	Percent of Observations
New	159	29.0%	1510	15.3%
Returning	390	71.0%	8371	84.7%
TOTAL	549	100.0%	9881	100.0%

```
                                   Number of Observers

     Midpt    Freq
     5.000     505 **********************************************************************************************************************(continues)
    15.000     139 **********************************************************************************************************************(continues)
    25.000      87 ***************************************************************************************
    35.000      61 *************************************************************
    45.000      47 ***********************************************
    55.000      28 ****************************
    65.000      26 **************************
    75.000      26 **************************
    85.000      17 *****************
    95.000      17 *****************
   105.000      12 ************
   115.000      12 ************
   125.000       8 ********
   135.000       9 *********
   145.000       3 ***
   155.000       3 ***
   165.000       2 **
   175.000       5 *****
   185.000       2 **
   195.000       5 *****
   205.000       5 *****
   215.000       2 **
   225.000       5 *****
   235.000       3 ***
   245.000       0
   255.000       3 ***
   265.000       1 *
   275.000       3 ***
   285.000       2 **
   295.000       6 ******
   305.000       0
   315.000       0
   325.000       3 ***
   335.000       0
   345.000       5 *****
   355.000       1 *
   365.000       1 *
   375.000       3 ***
```

Number of Observations

Figure 1. Frequency distribution of the number of observations per observer in the NADP/NTN Network, July 1978 through January 1986.

```
                        Number of sites

          Midpt     Freq
          0.500       41 *****************************************
          1.500       51 ***************************************************
          2.500       39 ***************************************
          3.500       29 *****************************
          4.500       15 ***************
          5.500       12 ************
          6.500        0
          7.500        2 **
          8.500        0
          9.500        1 *
```

Number of Observers

Figure 2. Frequency distribution of the number of observers per site in the NADP/NTN Network, February 1986-January 1987.

SECTION 8
Instruction Manual For NADP/NTN Site Operation

INSTRUCTION MANUAL
NADP/NTN SITE OPERATION

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Acknowledgement

This manual was revised under the guidelines of the Methods Development and Quality Assurance Technical Subcommittee of the National Atmospheric Deposition Program. Contributors to previous versions and the current revision include Van C. Bowersox, Jacqueline Peden, Mark Peden and Gary J. Stensland of the Illinois State Water Survey; D. L. Sisterson and P. M. Irving of Argonne National Laboratories and Carol Simmons of the Natural Resource Ecology Laboratory at Colorado State University.

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Foreword

This manual is intended as a guide to operations at NADP/NTN collection sites. In addition to the sample collection procedures and maintenance functions, a description of the NADP/NTN monitoring program has been included so that those individuals collecting the samples can understand the rationale for the care required in executing the procedures.

As further experience is gained in field operations, it is expected that problems will arise which were not anticipated and that procedures may need to be modified in the future. Please forward comments and suggestions to the NADP/NTN Program Coordination Office at the Natural Resource Ecology Laboratory, Colorado State University, Ft. Collins, Colorado 80523.

The procedures outlined in this manual do not attempt to address safety problems that might be associated with the operation and servicing of a monitoring station. It is the responsibility of the operator and his supervisor to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to the implementation of these procedures.

Summary Of Revisions

This manual is the second revision to the original 1978, 'Field Observer Instruction Manual' by Richard Semonin and Herbert Volchock. The text has been updated to include NADP's cooperative monitoring effort with the National Acid Precipitation Assessment Program (NAPAP) and editorial changes have been made to update the manual and make it easier to use.

The manual acknowledges the following additions and changes in NADP/NTN Field Site Operation protocols:

	REVISIONS	DATE
1.	DRY-SIDE sampling is now optional. Sites that do not collect DRY-SIDE samples perform a special bucket cleaning step after each DRY-SIDE bucket change. It should be noted that DRY-SIDE bucket removal still follows an eight week schedule for all sites. Only the submission of the sample to the analytical laboratory is optional. Notification of DRY-SIDE bucket changes are mailed to sites by the analytical laboratory prior to the DRY-SIDE bucket change date.	12 JUN 84
2.	Section 3.2.1. has been expanded to include the previously recommended practice of cleaning the underside of the foam lid seal and of wiping off the collector roof and sensor. Sites are additionally asked to write the *Site ID, Date* and *Time Off* on the bucket lid at the time the bucket is removed from the collector.	21 JAN 81
3.	Section 3.2.4. (formerly 3.2.2.) non-standard collection practices have been limited. The practice of allowing samples to accumulate for multiple weeks when buckets can not be changed within 24 hours of the Tuesday 9:00 am target is no longer endorsed. Additionally, the compositing of snow samples is no longer recommended. Snow samples, are now handled like any other sample and should be mailed to the CAL no later than two days after they have been removed from the collector.	29 JUL 87
4.	Minimal routine maintenance practices have been added or moved to the Field Procedures section and troubleshooting and repair information has been expanded with the inclusion of two appendices covering the maintenance and repair of the Aerochem Metrics Collector and Belfort Rain Gage.	22 MAY 87
5.	TIME ZONE declarations on the Field Observer Report Form are no longer necessary. The time zone and daylight savings schedule of each site are now declared and recorded in the NADP/NTN data base at the time of site startup. Sites are now instructed to operate under local time year round.	29 AUG 83

	REVISIONS		DATE
6.	The FIELD OBSERVER REPORT FORM has been revised. Modifications include:		
	BLOCK 1:	The STATION ID has been changed to request the CAL ID instead of the Coordinator's ID. Some sites had a problem determining which ID identified their site.	29 JUL 86
	BLOCK 4:	Daylight savings check boxes have been eliminated.	29 JUL 86
	BLOCK 5:	Questions were made more specific in an attempt to better define the necessary weekly checks to be performed on the wet/ dry collector.	29 JUL 86
	BLOCK 9:	More QC information has been requested from the sites. This information allows cross-checking of analytical techniques and assurances that standard solutions used at each site remain uncontaminated.	29 JUL 86
	BLOCK 10:	Supplies furnished through the analytical laboratory have been increased. Notable additions include rain gage charts, rain gage ink and pH electrodes.	29 JUL 86
7.	Field chemistry procedures have been modified to reflect our increased knowledge of the techniques necessary to measure precipitation samples accurately, and to standardize the pH measurement procedures now that each site is provided a standard type of pH electrode. A conductivity QC check has been added to the procedures and the number of significant digits asked for in measurements of standards has increased. The old *pH check sample* is now called the *quality control check sample* to reflect its use as a quality control check in both the pH and conductance measurements.		29 JUL 86
8.	The program now *recommends* that the field pH calibration steps be performed each week whether or not there is a precipitation sample to be measured. This recommended practice will help to maintain electrode performance, especially at sites that do not have many weeks with measurable precipitation samples.		22 MAY 87
9.	The Blind Audit Program procedures have been deleted. Instructions specific to each Blind Audit submission accompany the Blind Audit Sample that arrives at each field site. A general explanation of the program is now given in its place.		
10.	The Section 7.0 Directory has been updated.		
11.	Appendices A and B have been revised.		

1.0. Introduction

1.1. Deposition: A Background

The emissions of air pollutants and their subsequent transport, transformation, and dispersal are profoundly changing the chemical climate of the earth. It is now recognized that substances deposited by wet and dry processes significantly influence the supply of both essential and potentially injurious compounds available to biological systems. The nutrient status, growth, and development of plants on land and in surface waters are influenced by the availability of these substances in the atmosphere. The health and reproductive capacity of domestic and wild animals and fish populations are similarly influenced by atmospheric trace constituents. Deposition of chemical substances from the atmosphere may be beneficial for certain agricultural and forested ecosystems when the addition of nutrient elements promote plant growth or the input of acids accelerate weathering of soil minerals. At the same time, deposition may be detrimental, causing stress in plants and animals, leaching of nutrients from soils, alteration of water and soil solution quality, or modification of the natural weathering and corrosion of structures and materials. Since precipitation is a very good scavenging agent for many substances (both solid and gaseous) in the atmosphere, changes in the chemical composition of precipitation are good indicators of change in atmospheric composition.

The amount of substances dispersed in the atmosphere and deposited in precipitation, aerosols, and gases is projected to increase still further. Thus, there is an increasing need for careful measurement of the amounts, nature, distributions, and biological effects of these substances. Such measurements are essential for responsible management of the agricultural, forest, and aquatic ecosystems of the United States and all of North America.

1.2. NADP/NTN Monitoring Program History and Objectives

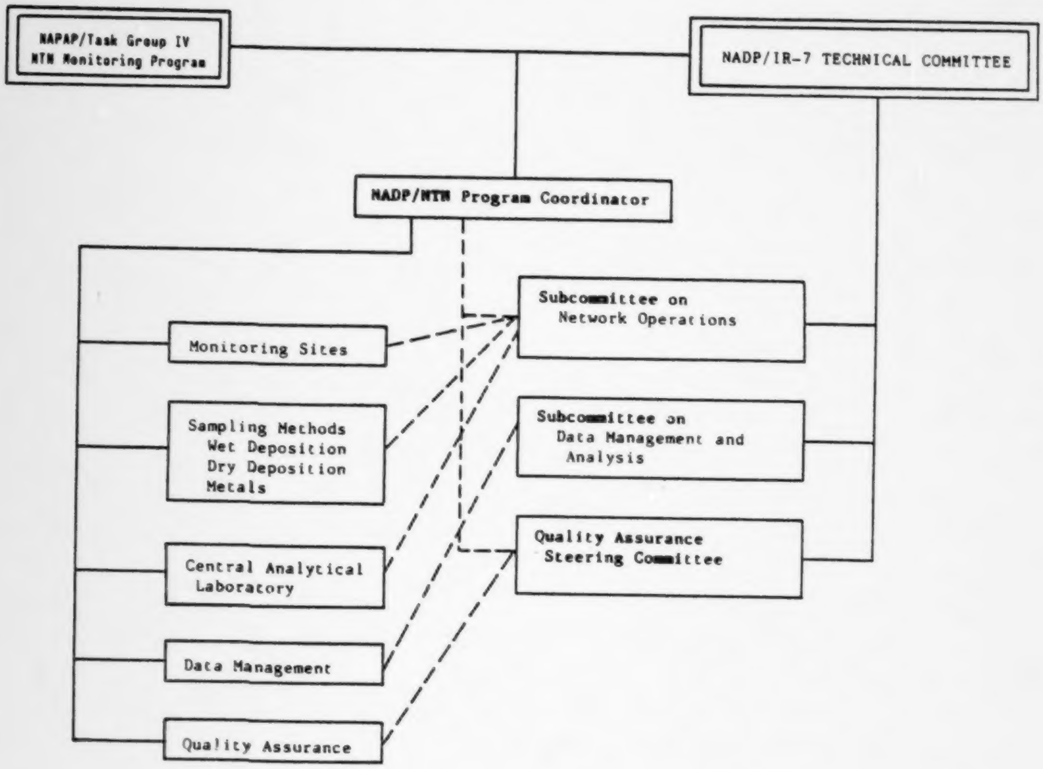
The National Atmospheric Deposition Program was organized in 1978 by the North Central Region of the State Agricultural Experiment Stations as Project NC-141 to address the problem of atmospheric deposition and its effects on agriculture, forests, rangelands and fresh water streams and lakes. In 1982 the program was endorsed by all four regions of the Association of State Agricultural Experiment Stations and subsequently became Interregional Project IR-7. The objectives of the NADP (IR-7) program are twofold:

1. To characterize the chemical composition of atmospheric deposition in North America and determine its spatial distribution and temporal trends through the establishment and maintenance of a nationwide network of monitoring stations. The network data will make possible the determination of trends in the supply of both beneficial and potentially injurious substances in precipitation and dry particulate matter deposited in various regions of the United States.
2. To promote and coordinate research on the effects of atmospheric deposition on terrestrial, aquatic, and materials resources. Areas of concern include: (a) the productivity of agricultural crops, forests, rangelands, wet lands, soils, and surface and ground waters; (b) the health and productivity of domestic food animals, wildlife, and fish; (c) atmospheric visibility and d) the degradation of materials and structures.

In 1980 the federal government established the National Acid Precipitation Assessment Program (NAPAP) to provide broadened support for research into the causes and effects of acid deposition. This program includes research, monitoring, and assessment activities directed towards providing a firm scientific basis for policy decision making. Due to its experience in designing, organizing, and operating a nationally distributed monitoring network, NADP was asked in 1983 to assume responsibility for coordinating the operation of the National Trends Network (NTN) of NAPAP. Since NADP and NTN had common siting criteria and operational procedures, and shared a common analytical laboratory, the networks were merged with the designation of NADP/NTN.

The network now stretches from Puerto Rico in the east to American Samoa in the west and operates in 47 of the 50 states. NADP/NTN research activities are supported by several agencies in addition to the original State Agricultural Experiment Stations. NADP/NTN receives support from the Department of Agriculture, the Department of Interior, the Environmental Protection Agency, the Department of Commerce and the Department of Energy. Additional support is provided by various state agencies, public utilities and industry.

Figure 1. Organization of The NADP/NTN Monitoring Program


NAPAP/Task Group IV
NTN Monitoring Program
NADP/IR-7 TECHNICAL COMMITTEE
NADP/NTN Program Coordinator
Subcommittee on Network Operations
Subcommittee on Data Management and Analysis
Quality Assurance Steering Committee
Monitoring Sites
Sampling Methods
Wet Deposition
Dry Deposition
Metals
Central Analytical Laboratory
Data Management
Quality Assurance

2.0. The NADP/NTN Monitoring Program

2.1. Site Selection: General Considerations

Collection sites for the Network are selected to give accurate and representative information concerning spatial, as well as seasonal, yearly, and other temporal variations in the chemistry of wet and dry deposition falling within major physiographic, agricultural, aquatic, and forested areas within each cooperating state and region. The sites are selected on the basis of available knowledge of sources of substances in the atmosphere, prevalent forms of deposition, frequency of precipitation events and other meteorological and atmospheric processes that influence the deposition of substances in each state or region. Wherever possible, collection sites are located in areas where watershed, marine, freshwater, or other hydrological research is already underway, or where research is being conducted on nutrient cycling, air pollution, or atmospheric chemistry. This permits the Network data to be compared with past records of precipitation chemistry maintained at some of these research installations. Protocols for establishing NADP/NTN monitoring sites are given in the *Instruction Manual for NADP/NTN Site Selection And Installation*. This document can be obtained through the NADP/NTN Coordination Office.

2.2. NADP/NTN Sampling Strategy

In establishing the Network, NADP and NTN have sought to ensure uniformity in commitment, in sampling protocol, and in analytical techniques and procedures. They agree that these are the ingredients essential to a successful network design and operation. To this end the NADP/NTN Monitoring Network has designated specific precipitation collection equipment to be used throughout the network which allows precipitation to be recorded, collected and verified (Appendix A). A strict weekly sampling protocol and a clear definition of sample types further makes comparisons between sites possible. The sample types and definition of the sampling periods are discussed in the following sections.

Additionally, every sample is analyzed at a single laboratory, the Central Analytical Laboratory (CAL) operated by the Illinois State Water Survey, Champaign, Illinois, for the following constituents: sulfate ($SO_4^=$), nitrate (NO_3^-), ammonium (NH_4^+), chloride (Cl^-), orthophosphate ($PO_4^\equiv$), sodium (Na^+), potassium (K^+), calcium (Ca^{++}) and magnesium (Mg^{++}). These constituents have been shown to be the major inorganic ions characterizing wet deposition. As overall indicators of precipitation quality, pH and specific conductance are measured at both the field sites and at the CAL. Finally, the entire program is monitored by external Quality Assurance Programs administered by the U.S. Geological Survey and the Environmental Protection Agency.

2.2.1. Sample Types

Atmospheric deposition has two components, wet and dry. Wet deposition includes all forms of precipitation (i.e. rain, snow, sleet and hail) and is characterized as a mixture of dissolved particles and gases, and undissolved particles in water. These substances are present at the parts per million level, or even lower. Dry deposition includes all forms of deposition that are derived from the net vertical transfer of chemical species to a surface, but that are not the result of precipitation. Dry deposition includes turbulent and gravitational settling, dew, frost and fog.

To separate the wet from the dry deposition components, scientists have for years employed samplers which automatically expose a wetfall container during precipitation and a dryfall container during all other times. This notion of a wet/dry collector is a compromise, since in no way does such a device exclude the dryfall that occurs during the course of a precipitation event. Fortunately, this compromise is generally not considered to be too serious, because the total deposition during a storm is dominated in most circumstances by the wet portion. As a matter of practice, then, the wetfall samples collected with a properly functioning wet/dry collector are considered to be wet-deposition-only.

The Aerochem Metrics Wet/ Dry Precipitation Collector used in the NADP/NTN Monitoring Network has two 3-1/2 gallon buckets which serve as the receptacles for wet and dry deposition. The bucket positions are designated WET and DRY on the instrument base. Between precipitation events the wet deposition bucket is covered by a motor-activated lid. When precipitation occurs, a sensor activates the motor which moves the lid from the wet deposition bucket to the dry deposition bucket. In the discussion that follows, samples will be referred to as WET-SIDE or DRY-SIDE, rather than Wet or Dry. This nomenclature avoids the confusion that might otherwise occur when a WET bucket contains no precipitation and is dry or a DRY bucket contains water. Definitions of the sample types used in the NADP/NTN Monitoring Network are given in Table 1. The definitions are further explained in the next sections.

Table 1. Sample Type Definitions

Sample Type	Definition
Wet-Deposition-Only Sample	A WET-SIDE sample that has been exposed only to precipitation and that has been protected from dryfall. Dry deposition exposures of less than 6 hours in any sampling period and less than 30 minutes at the end of any single event are considered insignificant.
Dry-Deposition-Only Sample	A DRY-SIDE sample that has never been exposed to precipitation. Dew, frost and fog may be incorporated in Dry Deposition Only Samples.
Bulk Sample	A WET-SIDE sample that has been exposed continuously to both wet and dry deposition for the entire sampling period.
Undefined Sample	Any WET-SIDE or DRY-SIDE sample that does not meet one of the above definitions.

Wet-Deposition-Only Sample Type

The Network has placed the highest priority on the collection of wet-deposition-only samples gathered from the WET-SIDE of the Aerochem Metrics Wet/Dry Collector. In the ideal case this sample type would contain 100% of the precipitation that occurred during a sampling period. During normal operation of the collector, however, small amounts of precipitation regularly appear in the DRY-SIDE bucket due to the collector's inability to sample some types of light dry snow and other trace precipitation events. In other instances an interruption of electrical power or other malfunctions may prevent the sampler from exposing the WET-SIDE bucket during precipitation. If the WET-SIDE bucket has been uncovered only during periods of precipitation and has never been exposed to dry deposition (periods of no precipitation) the term wet-deposition-only is used to describe the sample type. This designation is given even though some of the precipitation events might have been missed. The validity of the sample is not based upon the *amount* collected in the WET-SIDE bucket but rather, *in the ability of the precipitation collector to protect the sample.* The NADP/NTN monitoring program considers wet-deposition-only samples to be valid if the amount of exposure to dry deposition totals no more than 6 hours in any standard sampling period. Ideally, exposure should be limited to less than 30 minutes after the cessation of precipitation.

Dry-Deposition-Only Sample Type

A dry-deposition-only sample is collected from the DRY-SIDE of the Aerochem Metrics Wet/Dry Collector on those occasions when 100% of the precipitation events were collected by the WET-SIDE bucket. In practice the DRY-SIDE bucket usually contains small amounts of water and hence is not truly a dry-deposition-only sample. Dry-deposition-only samples are considered valid if their wet-deposition-only counterparts were collected from a properly working collector and they contain no more than a trace of liquid at the end of a standard sampling period. It should be noted that only grossly contaminated dry-deposition-only samples are invalidated by the Network.

Bulk Sample Type

A bulk sample occurs whenever a WET-SIDE bucket is exposed continuously to both wet and dry deposition for the duration of the sampling period. A bulk sample has never been covered during any part of the sampling period. This type of sample occurs when a collector fails to operate for an entire sampling period but sample buckets are continually changed weekly according to the NADP/NTN guidelines outlined in Section 3.2. Typically bulk samples are collected by manually positioning and then securing the lid of the collector over the DRY-SIDE bucket.

Undefined Sample Types

All other samples, not described above, are considered to be undefined sample types and are designated as invalid in the standard Network data base. These samples can occur when a collector fails during a sampling period, leaving the WET-SIDE bucket exposed to dry deposition; when the lid of a malfunctioning collector cycles continuously between the WET-SIDE and DRY-SIDE buckets during precipitation; when non-standard or modified equipment is used to collect an NADP/NTN sample, or when an operator fails to document collector operation adequately .

2.2.2. The Standard Sampling Period

The sampling period is the interval of time between bucket installation and bucket removal. In the absence of any operational failures of the collector, standard sampling periods are defined as follows:

WET-SIDE Sampling Period

WET-SIDE samples accumulate for one week. These buckets are removed from the collector and replaced at or about 9 AM (0900 local time) each Tuesday. If it is raining or snowing at collection time buckets are changed after the precipitation stops, but in no case later than midnight on Tuesday. WET-SIDE buckets are replaced weekly and sent to the Central Analytical Laboratory (CAL) even if no precipitation was collected during the sampling period. Dry WET-SIDE buckets are checked for the same ions as WET-SIDE samples that contain precipitation to assess the quality of the cleaning and handling of the bucket at the CAL and at the site, as well as to evaluate how well the collector seals the bucket from wind-blown dirt and debris.

DRY-SIDE Sampling Period

DRY-SIDE samples accumulate for eight weeks. At the end of each eight week period both the WET-SIDE and DRY-SIDE buckets are removed and replaced at the same time. Sites are notified as to the exact date prior to each DRY-SIDE bucket change. Unlike WET-SIDE samples DRY-SIDE sample collection follows one of the following options. DRY-SIDE options are declared at the time of site start up and are not routinely changed.

Option 1:

The DRY-SIDE bucket is replaced with a new CAL cleaned bucket and shipped along with a completed Field Observer Report Form to the CAL in the same manner as are the WET-SIDE buckets.

OR

Option 2:

The DRY-SIDE bucket is replaced with one of two *site-cleaned* buckets that are maintained at each site that follow this option. Site-cleaned buckets are clearly marked with the label 'DRY-SIDE ONLY'. The operator switches the buckets at the end of each eight week cycle. No DRY-SIDE bucket Field Observer Report Form is sent to the CAL under this option.

Following this standard protocol results in 52 (or possibly 53) WET-SIDE samples submitted for analysis per year. For sites sampling DRY-SIDE buckets, the protocol produces an additional 6 or 7 DRY-SIDE buckets. Every NADP/NTN site contracts then for the analysis of 52 - 59 samples per annum. All questions concerning contracting for chemical analysis or field site administration should be directed to the NADP/NTN Coordination Office.

2.3. Management of NADP/NTN Sites

The NADP/NTN monitoring network is an association of sponsored monitoring locations, that have been volunteered and equipped to meet the objectives of the National Atmospheric Deposition Program, the National Trends Network and oftentimes also local research goals. Sponsors include federal, state and other public and private research organizations as well as public utilities and private industry. As a part of this volunteered effort, two positions are typically identified at each site to perform the day to day tasks required by the network and to coordinate site operations with sponsoring agencies.

2.3.1. The Site Operator

The Site Operator is the person primarily responsible for the day to day operation of the NADP/NTN monitoring equipment and for the weekly collection and submission of precipitation samples and sample documentation. Site operators typically perform routine maintenance and repairs on site equipment, conduct field chemistry measurements on aliquots of the collected weekly precipitation sample and read, complete and interpret the weekly Field Observer Report Form and Rain Gage Chart associated with each weekly precipitation sample.

2.3.2. The Site Supervisor

Site Supervisors are responsible for overseeing site operations and for ensuring that NADP/NTN sampling and siting protocols are followed. Site Supervisors typically review the weekly data produced at the site, assist the Site Operator in troubleshooting operational problems and work to make resources available to the Site Operator by coordinating with the agencies that cooperate to operate the monitoring site.

2.4. Technical Support of NADP/NTN Monitoring Sites

Four organizations operate within the NADP/NTN monitoring program to provide technical support to NADP/NTN monitoring sites. The groups include the NADP/NTN Central Analytical Laboratory, the NADP/NTN Program Coordination Office and two external auditing agencies -the U.S. Geological Survey's National Water Quality Laboratory in Denver, Colorado and the Research Triangle Institute in Research Triangle Park, North Carolina. Support from these organizations ranges from troubleshooting of operational problems via telephone to reviews and performance evaluations which provide sites with information about their performance as compared to that of other stations. Figure 2 displays these organizations and illustrates their relation to one another.

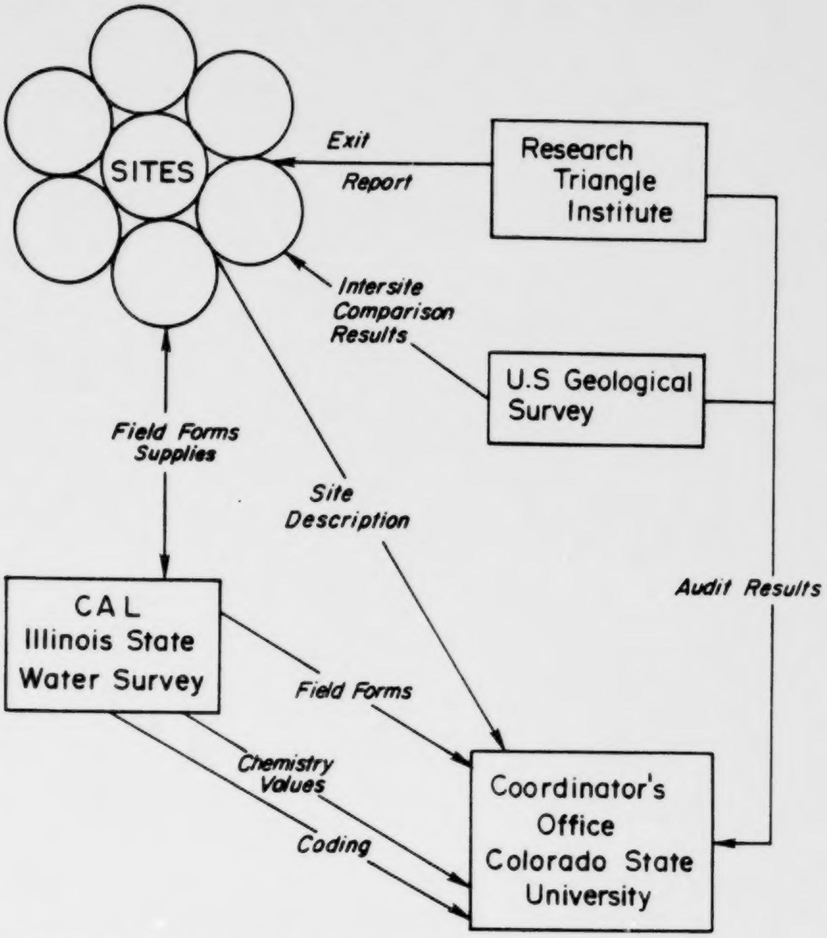
2.4.1. The Central Analytical Laboratory

The Central Analytical Laboratory (CAL) provides sites with the expendable supplies necessary for the normal operation of a monitoring site. It also provides the site with copies of preliminary analytical results, quality control checks, and verified data that originate from the Field Observer Report Form and Rain Gage Chart submitted each week by the site. Most importantly the CAL provides full-time troubleshooting of operational problems via telephone to site personnel. Finally, CAL offers periodic training for Site Operators.

2.4.2. The NADP/NTN Coordination Office

The NADP/NTN Coordination Office provides sites with troubleshooting for siting, equipment installation, and budgeting problems. It also provides sites with replacement components for monitoring equipment, final quality assured NADP/NTN data and all forms of Network documentation. The office is additionally responsible for coordinating site activities between all four organizations.

Figure 2. Technical Support of Field Site Operations


SITES
Exit
Report
Research
Triangle
Institute
Intersite
Comparison
Results
U.S Geological
Survey
Field Forms
Supplies
Site
Description
Audit Results
CAL
Illinois State
Water Survey
Field Forms
Chemistry
Values
Coding
Coordinator's
Office
Colorado State
University

2.4.3. External Audit/Review Programs

Two Federal agencies provide external quality assurance verification of the success of NADP/NTN field site operations. Results of these audits/reviews by the U.S. Geological Survey and Research Triangle Institute provide sites with assurances of the validity of NADP/NTN methods for field chemistry measurements and verification that operating protocols are being followed. Both agencies issue periodic reports which may be obtained through each agency or through the NADP/NTN Coordination Office.

3.0. Observers Instructions For Operating An NADP/NTN Monitoring Site

3.1. Requirements for the Collection of Wet and Dry Deposition

Because the success of the NADP/NTN monitoring network depends upon each site's continuing commitment to strictly follow the procedures outlined in this manual, the acceptance of a site into the Network is based in part on the site's ability to implement these procedures. Acceptance also assumes a commitment by each site to adhere to the following general guidelines:

- Each site is expected to operate continuously for a 5-10 year period.
- Sites will use the precipitation collection equipment listed in Appendix A to gather wet and dry deposition samples for the program.
- Sites will maintain this equipment in good working order at the original location specified on the SITE DESCRIPTION QUESTIONNAIRE submitted to the NADP/NTN Program Coordination Office. Sites will also maintain the area surrounding the collector as specified in the *Instruction Manual for NADP/NTN Site Selection And Installation.*
- Changes or modifications at the site or to its equipment will be submitted to the Program Coordination Office prior to implementation and documented in the REMARKS block on the FIELD OBSERVER REPORT FORM. This includes moving the site, siting other equipment in close proximity to the existing NADP/NTN samplers (30 meters), installation of snow roofs or event recorders, etc. See also the *Instruction Manual for NADP/NTN Site Selection and Installation.*
- Sites will adhere to the weekly Tuesday to Tuesday sample collection schedule, following the procedures outlined in this manual, and submit these samples with a completed FIELD OBSERVER REPORT FORM and RAIN GAGE CHART to the CAL at the Illinois State Water Survey, Champaign, Illinois for analysis.

In some instances when these guidelines are not followed, data sets and sometimes entire sites must be sequestered in the Network data base in order to maintain the integrity and quality of the Network data. It is hoped that this manual and the following guidelines will help to keep these occurrences to a minimum.

3.2. Field Procedures

The primary responsibility of the site operator is to submit a weekly, representative, wet deposition sample to the Central Analytical Laboratory. This manual has been prepared to assist each operator in this effort. It details the procedures for removing samples from the collector, maintaining the sample's representativeness, servicing the Aerochem Metrics wet/dry collector and Belfort rain gage, chemically analyzing the sample, and for gathering and transferring sample documentation to the Central Analytical Laboratory and Program Coordination Office. In order that the procedures outlined below are carried out in a careful and orderly manner, it is recommended that site personnel allocate 4 hours each Tuesday to these tasks.

3.2.1. General Considerations

The changing of buckets on the Wet/ Dry collector requires that a complete bucket mailer (black box with packing, lid, bucket and plastic bags) and indelible ink marker be brought to the field. In addition, the servicing of the rain gage requires that a new rain gage chart, and in some instances ink, be brought to the field.

Each mailer that is received should be immediately checked to verify that all of the supplies that will be needed for processing a sample have been sent. The mailer should contain 1 clean bucket and lid each encased in its' own plastic bag, one 20 *cc* syringe and horse hair packing material. In addition, the mailer may contain preliminary field or laboratory data being returned for verification, and items previously requested in Block 10 of the FIELD OBSERVER REPORT FORM (Report Forms, pH buffers, quality control check solution, pH electrode, etc.).

At the end of the standard sampling period (See Section 2.2.2.) the sample bucket(s) is removed from the collector. Careful handling of equipment and samples to prevent contamination is extremely important because the dissolved substances naturally occurring in precipitation have very low concentrations and any additional contamination will cause erroneous results. For example, one drop of human perspiration will completely invalidate a sample for sodium, chloride, and possibly other ions. Even a fingerprint on the inside of a bucket or lid may contain more sodium than an entire sample.

3.2.2. WET-SIDE Bucket Changes

Carry a black mailer containing a clean bucket and lid, and a permanent ink marker to the field site. Approach the collector and work from the downwind side of the field site to minimize wind blown contaminants from entering the buckets.

Checks and Inspections To Be Performed:

1. Inspect the site and equipment for any damage.
2. Check the temperature of the sensor on the Aerochem Metrics collector by pressing a finger against the *sensor plate*. It should be cool unless the collector has been open within the last several minutes.
3. Inspect the contents of the DRY-SIDE bucket and note any water that may be present.
4. 'Short out' the *sensor grid* with water. DO NOT USE METAL TO SHORT THE GRID. Apply enough water to assure that the collector stays open for 5-10 minutes. After the collector has been open for 5-10 minutes, check to make sure the *sensor plate* is warm.
5. Allow the lid mechanism to move over and cover the DRY-SIDE bucket. Observe the movement of the lid. It should operate freely with little motor noise and rest snugly over the bucket.
6. Examine the contents of the WET-SIDE bucket for contamination.

Removal Of The Bucket From The Previous Week.

- At the Aerochem collector open the black shipping container and remove the new lid. Using the bag as a glove so as to minimize contamination, place the lid on top of the 'old' bucket. Remove the 'old' bucket and new lid from the collector.
- Write on the lid using the permanent marker the *Site ID*, the *Date and Time Off*, and note the presence of any soil, bugs, bird droppings, etc. as noted in step 6.
- Place the bucket and lid back into the plastic bag and secure it with the twist tie. Place the bagged bucket back into the shipping container and secure it will all four straps. The container packing material compressed onto the bucket lid should prevent the sample from leaking during transportation back to the field laboratory. The bagging prevents packing material fibers from contaminating the sample and documents any leakage that might occur.

Installation Of The Bucket For The Next Week.

- Place the new bucket on the collector and remove the plastic bag in which it was shipped. Be careful not to touch any of the inside surfaces of the bucket. *Buckets (and lids) are not to be removed from plastic bags until they have been placed on the collector.*
- Note the TIME of the bucket change. This TIME will be used to complete two different FIELD OBSERVER REPORT FORMS (See Section 3.3). On the previous week's FIELD OBSERVER REPORT FORM it is entered as the BUCKET OFF TIME. On the current FIELD OBSERVER REPORT FORM, it is used for the BUCKET ON TIME of the sample bucket just installed. If replacing both a weekly WET-SIDE and an eight week DRY-SIDE bucket, be sure to label which bucket is removed from which side.

Final Aerochem Metrics Collector Checks.

7. Walk over to the recording rain gage and while the collector is open (the WET-SIDE bucket is exposed) check to make sure the *event recorder pen* is up. The up position indicates the correct operation of the motor box.
8. Confirm that the sensor heater is warm and then blow any remaining water off the sensor and observe the lid movement as it covers the WET-SIDE bucket. The lid should move smoothly and complete its cycle in approximately 15 seconds. Check to make sure the lid fits snugly over the bucket.

If the collector has failed to perform in any of the checks listed above (2, 4, 5, 7 or 8) try to use the troubleshooting guide in Appendix C to diagnose and resolve the problem. Contact the Central Analytical Laboratory for additional help and to determine which, if any, components may require replacement and which, if any, additional samples may have been affected.

If the collector has failed any one of the previous sensor or motor box checks, you may be required to place the collector into a bulk sampling mode (See Bulk Sample Type, Section 2.2.1)

Transportation Of The Sample To The Field Laboratory.

- Carefully transport the sample back to the field laboratory. If any of the sample is spilled or if the bucket is accidently dropped note this on the FIELD OBSERVER REPORT FORM along with your opinion as to whether the sample could have been contaminated.

Collection Of A Bulk Sample.

Method A

If the collector ***motor box*** will move the lid, activate the sensor. When the lid is on top of the DRY-SIDE bucket and just starting to compress the *foam pad*, unplug the collector.

Method B

If the collector ***motor box*** will NOT move the lid, reach down underneath the main frame of the collector and push the ***clutch arm*** counter-clockwise. The clutch will disengage (a little effort may be required) and the lid mechanism will be free of the drive system. Manually position the lid over the DRY-SIDE bucket and use the ***bucket retaining springs*** to secure the lid. Finally, unplug the collector to prevent an unexpected reactivation of the motor box from engaging the lid mechanism.

3.2.3. DRY-SIDE Bucket Changes

DRY-SIDE bucket changes occur at eight week intervals and are required of all sites - even those that are not collecting DRY-SIDE samples. It is only the submission of the DRY-SIDE sample to the CAL that is optional. Prior to each scheduled DRY-SIDE bucket change, the CAL notifies each site by letter of the exact change date and protocol options. Protocol Options are given in Section 2.2.2. under DRY-SIDE Sampling Period.

Replacement Of The DRY-SIDE Bucket.

- Use the same lid and bucket handling procedures discussed for WET-SIDE buckets for the DRY-SIDE buckets submitted for analysis (See section 3.2.2.), documenting times and all potential contamination on the lid.
- Additionally note all DRY-SIDE bucket changes on the corresponding WET-SIDE Field Observer Report Form.

Maintenance Performed During DRY-SIDE Bucket Changes:

While both buckets are being changed and if weather conditions permit:

a) With both buckets removed from the collector, use a clean sponge soaked in distilled or deionized water to wipe the underside of the polyethylene foam lid seal. The sponge should remove any accumulated dust and dirt; (Kimwipes[1], Kimtowels or a clean lint free cloth can be used if a sponge is not available).

b) After cleaning the underside of the lid, wipe the top side of the roof and sensor to remove bird dropping or other accumulations that could be blown into the sample bucket from these surfaces.

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[1] Kimwipes and Kimtowels are registered trademarks of the Kimberly-Clark Corporation, Roswell Georgia 30076.

c) After the polyethylene foam lid seal has air-dried, reinstall clean WET-SIDE and DRY-SIDE buckets in the collector.

d) Note which surfaces have been cleaned on the FIELD OBSERVER REPORT FORM.

3.2.4. Special Considerations

Any time a bucket is installed on or removed from the collector on a day other than Tuesday, or, any time a WET-SIDE bucket is not left in place for seven days, or, a DRY-SIDE bucket is not left on for eight weeks, a non-standard sampling period is produced. Non-standard sampling periods might occur when a collector is undergoing repair of essential collector parts, when the site becomes inaccessible because of severe weather conditions, or when regular or substitute personnel are unavailable to replace the buckets and service the rain gage. These occasions should be very infrequent and should be avoided whenever possible.

Should a non-standard sampling period become unavoidable, the following priorities should be exercised to minimize the problems which will result from sampling over different periods:

- First, if the sample bucket can be replaced on Monday (preferably late in the day) or Wednesday (preferably early in the day) instead of Tuesday, this should be done in lieu of any other day.
- Second, if heavy rain or snow will fill, or have completely filled the bucket, the sample period can be broken into two short sampling intervals each with separate FIELD OBSERVER REPORT FORMS. If possible, the bucket should be changed just before it becomes full (about 9 inches of rainfall), especially if it is still raining. Both buckets should be shipped to the CAL. FIELD OBSERVER REPORT FORMS should be annotated to describe incidents where snow mounded over the bucket or where water may have been lost due to overflow.

It should be noted that the Network no longer recommends accumulating samples for an additional week (i.e. 14 day samples).

All other instances of non-standard sampling intervals are considered as cause for invalidating samples in summaries of NADP/NTN data. No matter which alternative becomes necessary, a *non-standard sampling period must be specially documented in the PRECIPITATION RECORD and REMARKS blocks on the field form. Section 3.3.2., Block 8, PRECIPITATION RECORD describes the special documentation required.*

NOTE:*All* samples collected from non-standard collection periods (i.e. sampling periods of other than 6, 7 or 8 days) are declared invalid in NADP/NTN data summaries. Additionally, samples from intervals of more than 16 days are not used in outlier tests conducted during network quality assurance steps.

3.2.5. Servicing the Belfort Recording Rain Gage (See also Appendix D)

1. Open the rain gage's sliding access door and move both pens up and down to mark their positions on the chart. Lift the pens from the chart by moving the pen shifter outward.
2. Remove the chart and *chart drum*. Note the TIME and DATE in the appropriate place on the chart. Check the event pen trace to be sure that the collector opened and closed with each precipitation event.
3. Rewind the *clock*.

4. Remove the catch bucket and empty it except during winter operation when it will be filled with antifreeze solution (See Section 5.3.1.). Replace the bucket.
5. Record the time of the chart change on the new chart and install it on the drum and clock mechanism. Return the pen shifter to its normal position and mark the beginning of the precipitation and event pen traces by moving the pens up and down.
6. If appropriate, rezero the rain amount pen. Adjustments to the baseline are usually not required and *should only be done when the rain gage catch bucket is dry* [2]. Adjustments to the pen after emptying a wet catch bucket usually result in the pen drifting below the zero line on the chart.
7. The ink level of each pen should be checked and refilled if necessary. Ink frequently absorbs water vapor in humid weather and can double its original volume. If the lines on the chart record are very light or smeared, the pen ink has possibly become diluted with water. Replace the diluted ink with fresh ink. Tissue paper can be used to absorb the ink out of the pen nibs.
8. As a final check, make sure both the event pen and the rain amount pen are recording properly.

Table 2. Summary of Field Procedures

Device	Procedures
Aerochem Collector	Inspect and check the sensor, motor box and lid seals. Replace the WET-SIDE or DRY-SIDE buckets.
Belfort Rain Gage	Wind, inspect and check the rain gage clock. Replace the rain gage chart and start the pens inking. Check and inspect the inking and event recorder function.
Both	Perform any final checks and resolve any collector or rain gage malfunctions. This may require help from the CAL and the initiation of Bulk sampling. Record TIME, DATE and contamination information on the sample bucket lid and Rain Gage Chart.

3.3. Completing the FIELD OBSERVER REPORT FORM

3.3.1. Preliminary Observations

The FIELD OBSERVER REPORT FORM (FORF) (Figure 3) provided to each site by the CAL, is used to record essential information for the interpretation of chemical analysis and precipitation data. The form may be completed with either ball point pen or a sharp pencil of medium hardness. Be certain recorded notations appear on all copies and that the form is completely filled out and legible. Incomplete or illegible forms require additional time to process and phone inquiries by the CAL to the site observer or site supervisor.

It is suggested that sites maintain a policy of filling out TWO FORFs each week. One should be completed using the information gathered at the field site for the week just ending. The other should be started for the week just beginning. This will allow substitute observers to complete the forms without errors caused by mix-ups in time reporting or record keeping.

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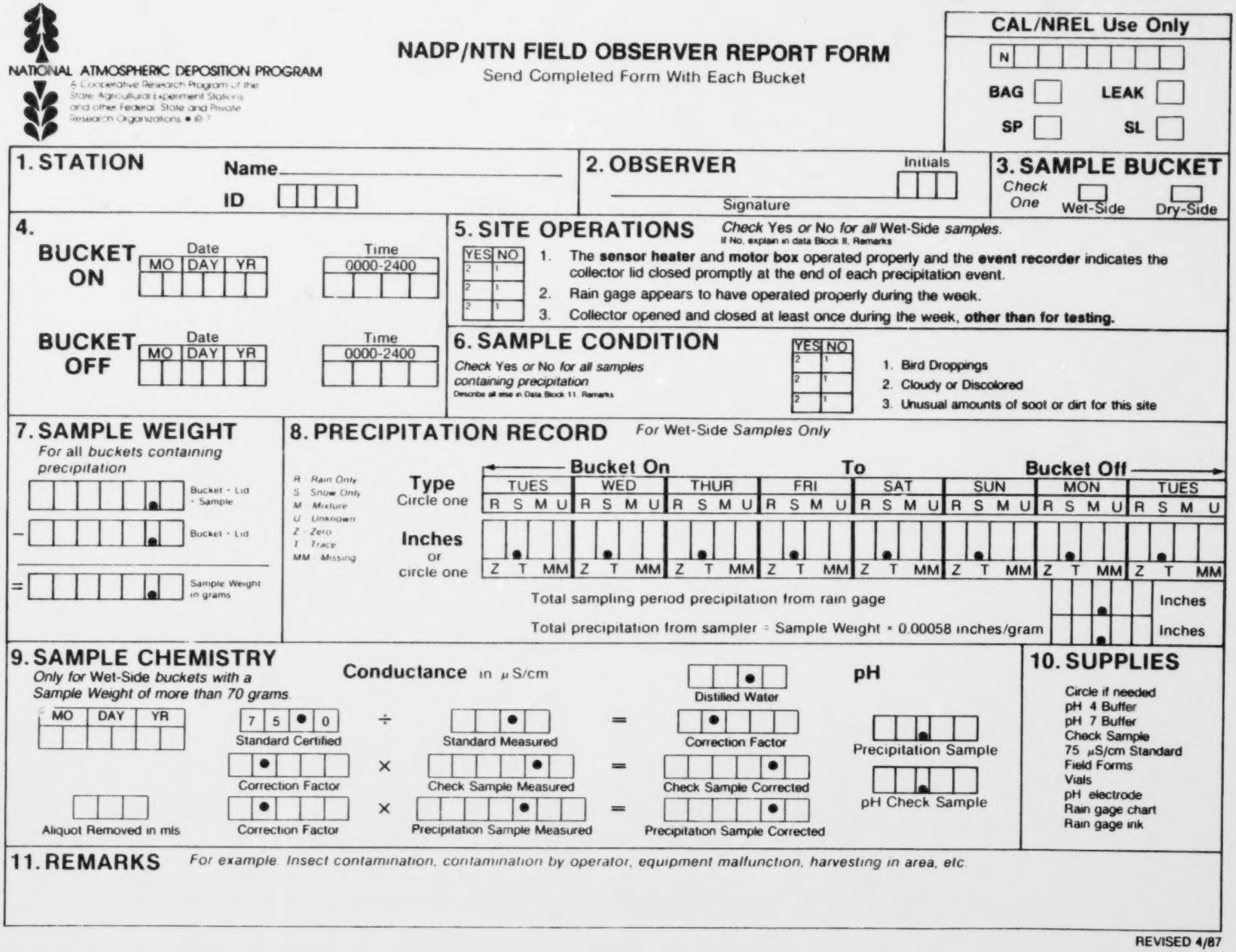
[2] The rain amount pen should never be rezeroed to remove the elevated baseline that results when the rain gage bucket is filled with anti-freeze during the winter months. It is further recommended that the baseline of the rain amount pen be set at approximately 0.15 to 0.25 inches during non-winter months. See Appendix D, Section D.1.3 for further details.

Figure 1. Field Observer Report Form



NATIONAL ATMOSPHERIC DEPOSITION PROGRAM
A Cooperative Research Program of the State Agricultural Experiment Stations and other Federal, State and Private Research Organizations • IR-7

NADP/NTN FIELD OBSERVER REPORT FORM
Send Completed Form With Each Bucket

CAL/NREL Use Only
N ☐☐☐☐☐☐☐
BAG ☐ LEAK ☐
SP ☐ SL ☐

1. STATION Name ____________
ID ☐☐☐☐

2. OBSERVER ____________ Signature Initials ☐☐☐

3. SAMPLE BUCKET Check One ☐ Wet-Side ☐ Dry-Side

4.

BUCKET ON Date MO ☐☐ DAY ☐☐ YR ☐☐ Time 0000-2400 ☐☐☐☐

BUCKET OFF Date MO ☐☐ DAY ☐☐ YR ☐☐ Time 0000-2400 ☐☐☐☐

5. SITE OPERATIONS *Check* Yes *or* No *for all* Wet-Side *samples.*
If No, explain in data Block II. Remarks

YES	NO	
2	1	1. The **sensor heater** and **motor box** operated properly and the **event recorder** indicates the collector lid closed promptly at the end of each precipitation event.
2	1	2. Rain gage appears to have operated properly during the week.
2	1	3. Collector opened and closed at least once during the week, **other than for testing.**

6. SAMPLE CONDITION
Check Yes or No for all samples containing precipitation
Describe all else in Data Block 11. Remarks

YES	NO	
2	1	1. Bird Droppings
2	1	2. Cloudy or Discolored
2	1	3. Unusual amounts of soot or dirt for this site

7. SAMPLE WEIGHT
For all buckets containing precipitation
☐☐☐☐☐☐•☐ Bucket + Lid + Sample
− ☐☐☐☐☐☐•☐ Bucket + Lid
= ☐☐☐☐☐☐•☐ Sample Weight in grams

8. PRECIPITATION RECORD *For Wet-Side Samples Only*

R · Rain Only
S · Snow Only
M · Mixture
U · Unknown
Z · Zero
T · Trace
MM · Missing

← Bucket On To Bucket Off →

	TUES	WED	THUR	FRI	SAT	SUN	MON	TUES
Type Circle one	R S M U	R S M U	R S M U	R S M U	R S M U	R S M U	R S M U	R S M U
Inches or circle one	☐•☐☐	☐•☐☐	☐•☐☐	☐•☐☐	☐•☐☐	☐•☐☐	☐•☐☐	☐•☐☐
	Z T MM	Z T MM	Z T MM	Z T MM	Z T MM	Z T MM	Z T MM	Z T MM

Total sampling period precipitation from rain gage ☐☐•☐☐ Inches
Total precipitation from sampler = Sample Weight × 0.00058 inches/gram ☐☐•☐☐ Inches

9. SAMPLE CHEMISTRY
Only for Wet-Side buckets with a Sample Weight of more than 70 grams.
MO ☐☐ DAY ☐☐ YR ☐☐

Conductance in μS/cm

7 5 • 0 Standard Certified ÷ ☐☐☐•☐ Standard Measured = ☐•☐☐☐☐ Correction Factor
☐•☐☐☐☐ Correction Factor × ☐☐☐☐☐•☐ Check Sample Measured = ☐☐☐☐☐•☐ Check Sample Corrected
☐•☐☐☐☐ Correction Factor × ☐☐☐☐☐•☐☐ Precipitation Sample Measured = ☐☐☐☐☐•☐ Precipitation Sample Corrected

☐☐☐•☐ Distilled Water

☐☐☐ Aliquot Removed in mls

pH
☐☐•☐☐ Precipitation Sample
☐☐•☐☐ pH Check Sample

10. SUPPLIES
Circle if needed
pH 4 Buffer
pH 7 Buffer
Check Sample
75 μS/cm Standard
Field Forms
Vials
pH electrode
Rain gage chart
Rain gage ink

11. REMARKS *For example: Insect contamination, contamination by operator, equipment malfunction, harvesting in area, etc.*

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Blocks 1-4 should be completed for all WET- and DRY-SIDE samples. Other blocks are completed only for those buckets indicated by the general block instructions.

STATION Block 1:

Fill in the STATION NAME and I.D. as assigned by the Central Analytical Laboratory (CAL). The STATION I.D. is a four character code also known as the CAL code. The code uniquely identifies your site location by state and in some cases county and/or town.

OBSERVER Block 2:

The OBSERVER SIGNATURE and INITIALS reported should be those of the person who fills out the form and performs the weekly sampling and field laboratory analysis even if he is only substituting for the regular observer. If more than one person is involved in these tasks, the signature and initials should be those of the person to whom communications concerning this sample and this week's site operations should be directed. Use three initials whenever possible.

SAMPLE BUCKET Block 3:

Check the box indicating the side of the sampler from which the bucket was removed. If the bucket is from the side marked Wet, check WET-SIDE, even if no precipitation has occurred and the bucket is dry. Similarly, a check in the DRY-SIDE box does not require that the bucket be dry.

Very small amounts of water or snow in the DRY-SIDE bucket can be expected. Dew, fog, light drizzles and/or snow flurries at times are not 'heavy' enough to trigger the operation of the collector. Large amounts of water in the DRY-SIDE bucket, however, indicate the collector has malfunctioned, perhaps because of a power failure or perhaps due to more serious electrical/mechanical difficulties. This type of malfunction should be noted in Block 5, SITE OPERATIONS and in Block 11, REMARKS.

BUCKET ON/OFF Block 4:

The DATE ON (month/day/year) and local TIME should be entered when the sample bucket(s) is installed (BUCKET ON) and then again when it is removed (BUCKET OFF) (See Section 3.2.2.). In both cases 24-hour TIME should be specified. 24-hour time runs from midnight to midnight (0000 hrs-2400 hrs) where noon is 1200 hrs. Therefore 9:00 AM would be 0900 hrs and 5:00 PM would be 1700 hrs. Declarations of standard or daylight-savings time are not necessary. Time zone declarations are made at the time of site startup and are maintained in the network data system.

SITE OPERATIONS Block 5:

Complete for all WET-SIDE samples.

Check YES or NO for each question. The answers to these questions and the comments provided in the REMARKS block are used to decide whether the sample has a definable type as outlined in section 2.2.1. and whether the general sampling requirements outlined in section 3.1. have been met. Since the operator is the one who observes the operation of the equipment in the field, it is important to obtain his assessment of the equipment's performance over the sampling period. For Questions 1 and 2 a YES response indicates correct site operation while a NO response indicates problems which must be documented in the REMARKS block.

Question 5.1 targets the Aerochem collector and is used to determine if the checks performed during the bucket changing uncovered any malfunctions in the sensor heating devices, drive or switching components, or event pen.

Question 5.2 targets the Belfort Rain Gage to determine if the clock performed accurately during the time period and to indicate that the pens traced effectively on the chart.

Question 5.3 attempts to identify samples which can be used as NADP/NTN site-specific system blanks. A response should only be made if your station is equipped with a *properly working event recorder*. Without the event marker information, dry WET-SIDE samples which qualify as system blanks cannot be distinguished from those exposed to dry deposition or light rain during the sampling period. The NO response identifies samples which may qualify. (Note: Test or servicing events should not be used to indicate a YES response).

Dry WET-SIDE sample blanks are analyzed for all of the normal parameters and serve as contamination checks on such steps as human handling at the CAL and the site, bucket washing at the CAL, and the ability of the Aerochem Metrics Wet/Dry Collector cover to seal the bucket at the site.

SAMPLE CONDITION Block 6:

Complete for all samples that contain precipitation.

The SAMPLE CONDITION boxes provide qualitative information about the sample that might not otherwise be obtained if not recorded by the observer. These observations should be made at the time the WET-SIDE bucket (or in some cases when liquid is present in the DRY-SIDE bucket) is changed, ideally before the bucket is agitated, and before the lid is placed on the bucket.

Checking the appropriate box YES or NO and providing additional comments in BLOCK 11, REMARKS will help determine the degree of particulate matter and contamination in the sample at the time of collection. Contamination of the sample reported by the site operator may indicate the sample should be sequestered from other standard samples in the NADP/NTN data base. Bird droppings, for example, are a gross contaminant that become homogenized in transit and are sometimes not visible in the sample when it arrives at the CAL. Other gross contaminants, especially insects, should be documented in the REMARKS, Block 11.

Never attempt to remove any contaminant, no matter how large, from a bucket, WET or DRY.

SAMPLE WEIGHTS Block 7:

All samples that contain water must be weighed. This includes samples from the WET-SIDE and the DRY-SIDE of the Aerochem Metrics Wet/Dry Collector.

In the field laboratory, remove the bucket from the shipping container and plastic bag. If any of the sample has spilled during the transporting of the bucket to the field laboratory, attempt to weigh it. First weigh the water and the bag and then the bag alone. Note this on the FORF in Block 11, REMARKS. *Discard the spilled water. Do not pour it back into the sample bucket.*

Carefully wipe any liquid or debris from the exterior of the sample bucket and weigh the sample including the lid to the nearest gram. The balance used for weighing the sample containers should have a 20 kg capacity and a sensitivity of 1 *g*, (see Appendix A). Record this weight as BUCKET + LID + SAMPLE in grams on the data form.

The original weights of the clean bucket and lid have been written on the side of the lid and bottom of the bucket and are added together as BUCKET + LID. Record the sum on the data form. The difference between these two weights (BUCKET + LID + SAMPLE minus BUCKET + LID) is the SAMPLE WEIGHT.

3.3.2. Interpretation of the Rain Gage and Event Recorder Chart

The weekly interpretation of the rain gage chart by the site operator provides the NADP/NTN monitoring program with two important pieces of information. First, the chart yields the the daily amounts of precipitation which are reported in PRECIPITATION RECORD, Block 8 on the FIELD OBSERVER REPORT FORM. The sum of these daily amounts should correspond to the volume of liquid present in the Aerochem Metrics Wet/Dry Collector. Secondly, the chart reveals the coincidence of Aerochem Metrics collector operation with precipitation events through the tracings of the Event Recorder. When differences in the amount of precipitation between the Rain Gage and the Aerochem Metrics Wet/Dry Collector are identified, the event record is used to determine where the discrepancy occurs and the significance of the difference. Large and persistent discrepancies should be reported to the CAL as soon as possible and in data block 11, REMARKS on the FIELD OBSERVER REPORT FORM.

Chart Features:

Figure 4 represents a sample rain gage chart with rainfall amounts (lower line) and an event recorder tracing (upper line). Like all weekly charts used in the NADP/NTN network it covers an eight day period. Scaling of the chart is in inches and is represented by the numbers printed along the major divisions of the chart; 1-11, 2-10, 3-9, etc. Since this chart is designed for a dual traverse rain gage the number printed before the dash represents the precipitation amount as the pen swings upward recording 0-6 inches of precipitation. The number after the dash represents additional precipitation as the pen swings downward recording 6-12 inches of precipitation. The boxed area of the chart is used to record the station ID and the charts' period of record (TIME ON/OFF and DATE ON/OFF).

Each vertical chart division represents 0.05 inches of precipitation. The maximum resolution of the chart is 0.01 inches but this depends upon the operator's ability to carefully evaluate the precipitation tracing. Each horizontal chart division represents two hours time. The maximum resolution is 15 minutes; however, this is also dependent upon the operator's interpretation skills. The resolution of the time axis is rarely critical since time data are only used to split the sampling period into daily parcels and to cross-reference the TIME ON and OFF of the Wet/Dry bucket.

In general, accumulating precipitation is recorded on the lower portion of the chart and the number and duration of Wet/Dry collector 'events' are recorded on the upper portion of the chart. For the purposes of interpreting the example precipitation record (bottom line), numbers have been added to the precipitation tracing to relate this tracing to the Wet/Dry collector events (top line). As designed the event recorder trace (top line) lags behind the precipitation record by ~ 4 hrs. This offset allows the rain gage pen to swing freely full scale 0-12 inches without interference from the event recorder pen.

Event Recorder Transcription

Because the event pen lags behind the precipitation pen the event pen tracing must be transcribed to the same time axis as the precipitation pen. This is done by laying the upper edge of the FIELD OBSERVER REPORT FORM against the upper event pen line and copying the event pen trace on to the edge of the FORF. The new event pen trace is then similarly transferred to the lower precipitation line such that the event pen tracing is super-imposed upon the precipitation line beginning at the same spot on the time axis.

Figure 4. Example NADP/NTN Rain Gage Chart

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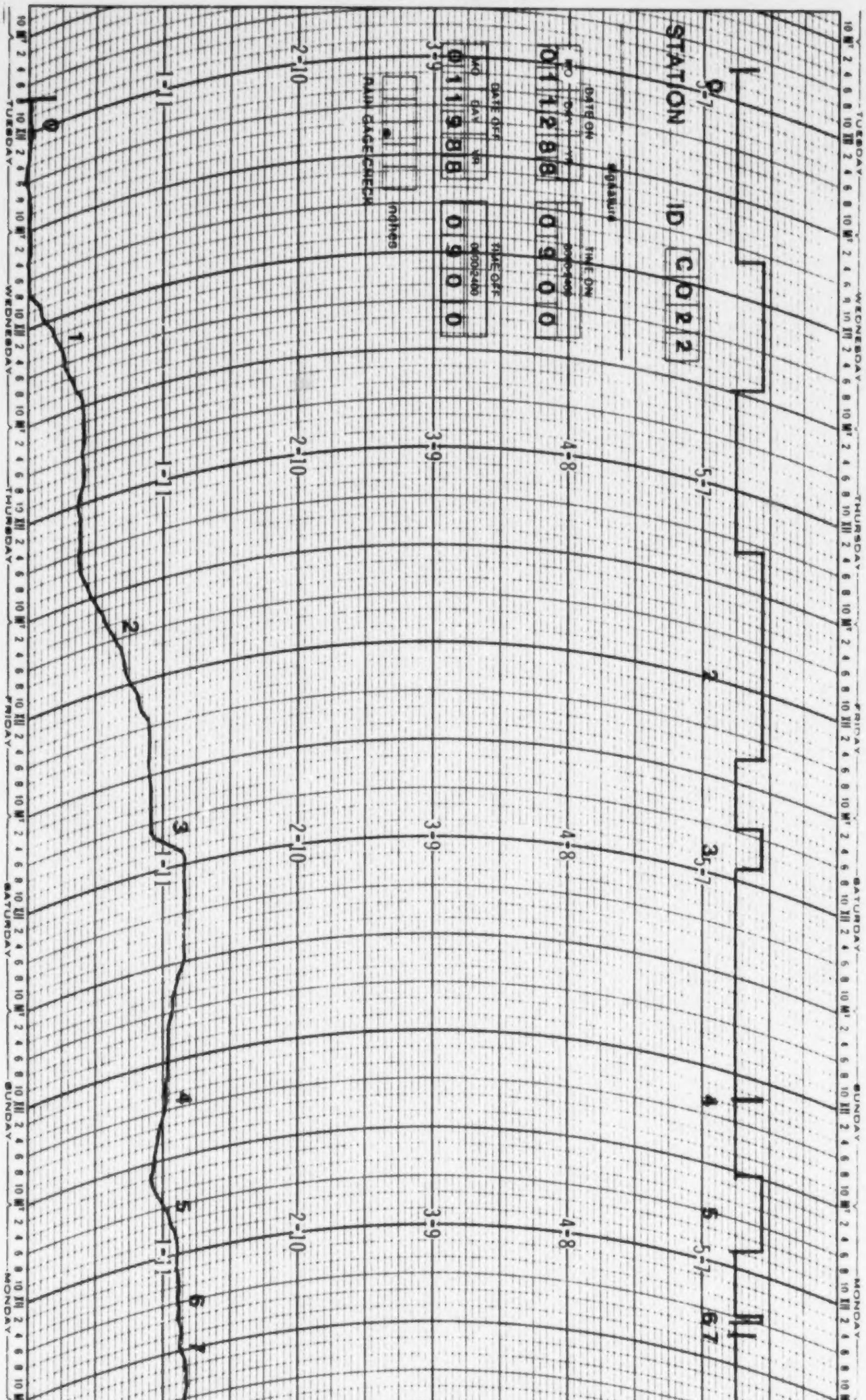
CHART NO. 5-4046-BI
12 INCH DUAL TRAVERSE 192 HOURS
UNIVERSAL RAIN GAGE
BELFORT INSTRUMENT COMPANY
BALTIMORE MARYLAND. U.S.A.



STATION ID C022

DATE ON MO DAY YR 01 12 88

TIME ON 0000-2400 0900

signature

DATE OFF MO DAY YR 01 19 88

TIME OFF 0000-2400 0900

RAIN GAGE CHECK . inches

NADP/NTN PRECIPITATION RECORD

Reading The Rain Gage Chart:

Starting at Tuesday's 0 numbered event, note that the baseline of the lower tracing drifts. Up to 0.05 inches of drift on the chart is normal and is usually a result of the sensitive mechanical linkage of the pen arm responding to daily temperature oscillations. The chart paper also expands and contracts due to changes in humidity. If a significant precipitation event had occurred, the event recorder would most likely have shown a deflection from the baseline. However, the lack of an event pen deflection does not guarantee that precipitation has not occurred. *Both lines and visual observations should be used to determine whether or not precipitation has occurred.*

Event 1 demonstrates how the event recorder works in relation to the precipitation amount. The event pen (top line) steps up sharply as the collector opens, corresponding to the start of the precipitation event, and stays up until the event is over. At the end of the event the tracing returns to its baseline position. The precipitation amount is measured from the start of the rise in the rain gage tracing (bottom line) to the end of the rise. This event then started about 8 a.m. on Wednesday and lasted until midnight, leaving 0.40 inches of precipitation. This is confirmed by the event recorder which also shows the event starting at 8 a.m. and stopping at midnight.

Event 2 precipitation is measured again from the start of the rise of the event to the end of the rise. It does not include the rise of event 1 and accounts for the dropping of the pen trace by about 0.03 inches between the finish of Event 1 and the start of Event 2. This difference may be due to drift or evaporation but in any case is not important to Event 2 or to Event 1. Remember, we are trying to determine the amount of rain that fell in the rain gage bucket for each rainfall event, not the amount that is still in the rain gage bucket. Again, the event recorder confirms the event.

Event 3 is like Event 2 and also is confirmed by the event recorder. Note, however, how the event recorder may more accurately indicate the start of the event. Since the rain gage has a resolution of approximately 0.01 inches, it is possible for the event recorder to display an opening before precipitation is sufficient to cause the rain gage pen to respond.

The interpretation of Event 4 requires that you understand exactly what the event recorder does. It records the time the wet bucket is exposed to deposition. It does not actually record the start/stop and duration of precipitation events. We only assume it records precipitation events based on the assumption the wet/dry collector opens for precipitation events. The event marker on Event 4 indicates that the Aerochem Metrics sampler did open, however, the rain gage tracing (bottom line) is inconclusive as to whether measurable precipitation did occur. Unless you have reason to believe otherwise, this should be recorded as a trace amount of precipitation. In this case the fact that the Aerochem Metrics Collector opened is just as important in determining the occurrence of precipitation as is the amount of precipitation recorded by the rain gage (See block 5, SITE OPERATIONS on the FIELD OBSERVER REPORT FORM).

Event 5 is similar to Events 2 and 3. This event better illustrates the sometimes dramatic fall of the rain gage tracing and its irrelevance to the determination of precipitation in Event 5 or 4 or 3. During Event 5, 0.21 inches of precipitation occurred.

Events 6 and 7 are similar to Event 4 and reflect the type of tracing that might occur during periods of intermittent drizzle or heavy fog. The collector opens frequently or stays open for a short time while no appreciable precipitation occurs.

Event 8 is not a precipitation event but rather a 'Test' event which occurs when the Aerochem Metrics sensor is activated by the operator to change the buckets. This type of event may appear at both ends of the sampling period depending upon when the rain gage chart is changed in relation to the WET-SIDE sample buckets.

Table 3 indicates the amount of precipitation for each event and the total for the week. The correct weekly total amount of precipitation can only be established by determining the amount of precipitation in each event and adding the amounts.

Rearranging Precipitation Events to Complete The Field Form:

To complete the PRECIPITATION RECORD block on the FIELD OBSERVER REPORT FORM, Table 3 event data must be rearranged into daily precipitation amounts. This is accomplished by adding events, as in Events 6 and 7, or splitting events, as in Event 2, to get the proper amounts of precipitation for each day. The correct daily amounts of precipitation are listed in Table 4. Finally, use the event recorder tracing to ascertain if and when events were missed or if the collector cycled continuously. Note these occurrences on Block 11 on the FIELD OBSERVER REPORT FORM.

Table 3. Chart Events

Event no.	Precipitation Amount
1	0.40
2	0.53
3	0.27
4	Trace
5	0.21
6	0.05
7	Trace
8	Test
Total	1.46

Table 4. Daily Precipitation

Day	Amount
Tuesday	0.00
Wednesday	0.40
Thursday	0.08
Friday	0.45
Saturday	0.27
Sunday	Trace
Monday	0.26
Tuesday	0.00
Total	1.46

3.3.3. Reporting Precipitation

The NADP/NTN uses precipitation information from both the Aerochem Metrics Wet/Dry Collector and the Belfort Recording Rain Gage to determine the amount of precipitation (and deposition) that fell during a given sampling period. The volume of precipitation in the WET-SIDE bucket (SAMPLE WEIGHT) is used as the basis for determining chemical analysis concentrations. It is also used to quantify any loss of sample that may have occurred during the shipment of the sample to the CAL. This value, however, represents only what fell into the bucket. When trace amounts of precipitation occur that do not trigger the collector sensor, when power outages occur, or when the sampler malfunctions, this measurement will not represent the true precipitation amount for the sampling period.

The rain gage is used to determine the true amount of precipitation that fell during a sampling period. This amount together with the chemical concentrations from the Wet/Dry

Collector is used to calculate deposition. When precipitation exceeds 0.50 inches, the amount of precipitation collected by the Aerochem Metrics Collector and the Belfort Rain Gage should agree within 15%. Differences greater than 15% may indicate sampler malfunctions or rain gage calibration problems. Other factors, such as high winds and/or blowing snow may also cause disagreements between the collector and gage.

PRECIPITATION RECORD Block 8:

The PRECIPITATION RECORD must be completed for all WET-SIDE samples, and must match the DATE ON and DATE OFF listed in data Block 4. If the sampling period is longer than one week or starts or stops on a day other than Tuesday, additional FIELD OBSERVER REPORT FORMS must be completed to make the PRECIPITATION RECORD match the format of the FORM. One form should be completed for each week or fraction thereof represented within the sampling period. If a shorter period results, simply cross out those days that are not relevant.

PRECIPITATION TYPE

The type of precipitation should be circled for each day precipitation occurred. Circle R if only rain occurred, S if only snow occurred, and M for any combination of the above including sleet and freezing rain. Use U for unknown, for those instances when you do not know the precipitation type. Hail should be considered as rain (TYPE R), but additionally documented in the REMARKS block.

Fog, dew, and frost are not considered to be precipitation and as such should not be reported as trace amounts of precipitation. They should, however, be noted in Block 11, REMARKS.

PRECIPITATION AMOUNTS

Record the amount of precipitation from the rain gage chart for each day to the nearest one hundredth of an inch (two decimal places) (See Section 3.3.2.). On the first Tuesday (or day) of the sampling period, report only the precipitation that occurred after the bucket was installed. If no precipitation occurred circle Z in the box immediately below the amount for that day. Likewise if you do not know the amount of precipitation circle MM to indicate that it is missing or unknown. Annotate the REMARKS Block to describe the reason for the missing amounts (i.e. clock stopped, pen did not ink, etc.). If one of the daily values is a cumulative amount, this should also be annotated in the REMARKS Block. It is just as important that you indicate when precipitation did not occur as it is to indicate that precipitation did occur. The T is circled in those instances where a trace amount of precipitation occurred (less than .01 inches).

The bottom of the Precipitation Record block contains a place to record the TOTAL SAMPLING PERIOD PRECIPITATION FROM THE RAIN GAGE. This should be the sum of the daily precipitation amounts. If one or more of the daily amounts is missing, this value may be missing. The second line records the amount of precipitation in inches that fell in the collector (TOTAL PRECIPITATION FROM THE SAMPLER). This value is obtained by multiplying the SAMPLE WEIGHT in grams (from block 7) x 0.00058. If the collector and rain gage are operating properly and more than 0.50 inches of precipitation occurred during the sampling period the two values should agree to within 15%. If they do not agree, the CAL may be consulted for assistance.

3.3.4. Field Laboratory Analysis

- *If the SAMPLE WEIGHT measured in block 7 is less than 70 grams, omit the Sample CHEMISTRY Section and proceed to section 3.3.5., REMARKS, block 11.*

It is generally accepted that under certain conditions changes in the chemical composition of precipitation will occur between the time a sample is collected in the field and the time it is analyzed at a central laboratory. Accurate measurements of both specific conductance and pH by site operators are essential to demonstrate and document the phenomena when it occurs. It is also imperative that *Samples be shipped within 48 hours of their removal from the field.*

Before beginning the set of procedures described below it is important to keep in mind the following points:

- Standards and Check solutions should be stored in a cool dark place. Before any aliquots or measurements are taken they should be allowed to come to room temperature. Their formulations are designed to approximate the samples you are analyzing and to indicate to both you and the CAL when measurement problems occur. The solutions should be usable for up to one year if stored properly. If at any time however, you notice a change in the values you obtain for these solutions, or notice contamination, ask the CAL for a replacement.

- If a sample is frozen, allow it to melt and come to room temperature before proceeding. Aliquots should not be removed until the sample has completely thawed.

- Never return unused aliquots of standards or samples to their original containers. All unused portions of standards or sample aliquots should instead be discarded.

- Always determine specific conductance first. This is especially important when the same sample aliquot must be used to determine both specific conductance and pH.

- Distilled or deionized water used in these procedures must have a specific conductance of less than 2 μS/cm. Using water with a conductance greater than 10 μS/cm may result in contamination of your sample aliquot and the measuring electrodes.

- Space on the FIELD OBSERVER REPORT FORM is provided for one value of conductivity and pH. If the quality of the measurement is suspect, and the determination is repeated using the same aliquot, only the final value is recorded. If acceptable values for the pH or conductance standard solutions can not be obtained in the initial steps of the procedures, do not make the field measurements on the sample aliquot. Instead call the CAL for assistance. Appendix B provides additional information that may help in resolving pH and conductivity measurement problems. Problems should be mentioned in REMARKS, block 11.

- The instructions that follow apply to a wide variety of conductance and pH meters in a general manner. These instructions should not conflict with manufacturer's instructions for the calibration of their equipment. They should instead complement the manufacturer's instructions. To further ensure this, each operator should be familiar with the manufacturer's instructions for the calibration of their specific instrument.

SAMPLE CHEMISTRY Block 9:

If the SAMPLE WEIGHT measured in block 7 is less than 70 grams, omit the SAMPLE CHEMISTRY section and proceed to section 3.3.5., REMARKS, block 11.

> SPECIAL NOTE: It has been demonstrated that pH electrode performance improves with use. It is therefore recommended that you follow steps 1-5 of the pH Measurements section each week whether you have precipitation samples to measure or not. If you do follow these procedures each week, please include the results on the FIELD OBSERVER REPORT FORM.

If the SAMPLE WEIGHT measured in block 7 is 70 grams or more, remove a single $20mL$ aliquot of wet sample using the clean, disposable, calibrated syringe supplied with each sample collection bucket. In order to avoid contamination, be careful not to touch the tip of the syringe when removing the syringe cap, or the inner surface of the bucket when removing the aliquot. After removing the aliquot, replace the cap on the tip of the syringe and store the sample in the syringe until you are ready to make your measurements. *In no case should an aliquot greater than 20mLs be removed from the bucket.*

Once the aliquot has been removed secure the lid to the bucket. Press the lid onto the the bucket gasket side down. Then starting at the 12 O'clock position, pound the lid on the mold scars with a rubber mallet. Visually inspect the seal to see if the lid and bucket rims are parallel. Test the seal by running your finger around the perimeter of the lid feeling for any gap between the lid and bucket.

Record the DATE and TIME of the field laboratory analysis on the FIELD OBSERVER REPORT FORM as well as the milliliters of the ALIQUOT REMOVED.

Conductance Measurement

Standardize the Meter and Cell

1. Rinse your conductance cell at least three times with distilled or deionized water. Rinse once with the 75 $\mu S/cm$ standard. Using a second portion of standard, measure the specific conductance of the 75 $\mu S/cm$ standard.
2. If your conductance meter has a calibration control, standardize your instrument according to the instruction manual using the 75 $\mu S/cm$ standard solution supplied by the CAL. Record the value to the nearest 0.1 $\mu S/cm$ in the space marked STANDARD MEASURED.

   If your meter does not have a calibration control, record the value obtained in step 1 to the nearest 0.1 $\mu S/cm$ in the space marked STANDARD MEASURED.
3. Calculate the CORRECTION FACTOR to the nearest 0.001 by dividing the STANDARD CERTIFIED (75.0 $\mu S/cm$) by the STANDARD MEASURED. Record this value in the three spaces marked on the form.

Measure the Conductance of Your DEIONIZED WATER

4. Rinse the cell three times with deionized or distilled water, discarding each rinse. Use a fourth portion to determine the specific conductance of your distilled or deionized water. Record the value as DISTILLED WATER on the data form to the nearest 0.1 $\mu S/cm$. This value should be the lowest reading you are able to obtain after repeated rinsings. The value should not exceed 2. If a value of more than 10 is measured do not continue with the measurements. Instead obtain a new supply of distilled or deionized water and repeat steps 1-4 before proceeding.

Measure the QUALITY CONTROL CHECK SAMPLE

5. Without rerinsing the cell, but shaking off the excess water, rinse the cell with the quality control check sample. Use a second portion to determine its specific conductance. Record this value to the nearest 0.1 $\mu S/cm$ as the CHECK SAMPLE MEASURED. Multiply this value by the CORRECTION FACTOR and record the result as the CHECK SAMPLE CORRECTED. This value should be 21.8 +/- 3.0 $\mu S/cm$. If the corrected value falls outside of these limits there is a potential measurement problem and the CAL should be contacted.

Measure the PRECIPITATION SAMPLE

6. Rinse the cell three times with deionized or distilled water, discarding each rinse. If the conductance cell is of the recommended small volume type (see Appendix A), next rinse the cell with approximately $3mL$ of the precipitation sample aliquot. Use a second 3-$4mL$ portion to determine the PRECIPITATION SAMPLE MEASURED. Record this value to the nearest 0.01 $\mu S/cm$. Multiply this value by the CORRECTION FACTOR to obtain the PRECIPITATION SAMPLE CORRECTED.

   If the conductance cell is not of the recommended type, shake off the excess deionized or distilled water from the third rinse and measure the necessary size portion of the precipitation sample to the nearest 0.01 $\mu S/cm$. Record this value as the PRECIPITATION SAMPLE MEASURED. Multiply this value by the CORRECTION FACTOR to obtain the PRECIPITATION SAMPLE CORRECTED.

Store the Conductance Cell

7. Rinse the cell three more times with deionized or distilled water, and then fill the cell with the water. Cover the cell with Parafilm[3] or an inverted sampling vial to prevent evaporation. Change the storage water weekly.
8. Retain the remaining precipitation sample aliquot in its original syringe (or a clean beaker if the same solution is to be used for pH) for further analysis.

pH Measurement

The Central Analytical Laboratory supplies a standard combination pH electrode to all sites. This is the only electrode to be used in making NADP/NTN field pH measurements. It should not be used for any other samples. Notify the CAL prior to making measurements if the use of another electrode becomes necessary. Replacement electrodes are available through the CAL. The CAL also provides small volume polystyrene sampling vials to be used for each pH measurement. Each vial should be rinsed with the solution it is to contain just prior to use. To keep the vials free of dust and contamination, store them in the bag in which they arrived.

Prepare the pH Meter and Electrode for Testing

1. Adjust the temperature control on the meter to room temperature. If no thermometer is available set the the temperature control to 25° C. Rinse the electrode several seconds in a flowing stream of deionized or distilled water. Make sure any accumulated salts are dissolved from the tip of the electrode. This build-up happens normally during storage. Unplug the fill hole at the top of the electrode and replenish the filling solution, *using only the filling solution provided by the CAL.*

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[3] Parafilm is a registered trademark of the American Can Corporation, Greenwich Connecticut.

Calibrate the pH Meter

2. Fill one of the small sampling vials with pH 7.00 buffer. Insert the electrode into the vial and allow it to remain there for 30 seconds. Dump the buffer out of the sample vial and without any other rinses, refill the vial with the 7.00 pH buffer. Insert the electrode tip directly into this *conditioned* vial of pH 7.00 buffer. Allow sufficient time for the reading to become stable -within 0.01 pH unit for 30 seconds. This step should take 3-5 minutes. Adjust the calibration or standardize control to read pH 7.00.

3. Rinse the electrode throughly with deionized or distilled water. Gently blot the electrode tip with a clean absorbent laboratory wipe such as Kimwipes or Kimtowels. Fill a clean vial with pH 4.00 buffer. Repeat the conditioning rinse as described in step 2 by inserting the electrode into the vial and allowing it to remain there for 30 seconds. Then, remove the electrode, dump the buffer, refill the vial and insert the electrode again. Allow sufficient time for the reading to become stable -within 0.01 pH units for 30 seconds. Adjust the slope control of the pH meter to read pH 4.00.

4. Rinse the electrode with deionized or distilled water. Gently blot the electrode tip with a clean absorbent laboratory wipe such as Kimwipes or Kimtowels. Repeat step 2. If the pH reads 7.00 +/- 0.03 pH units then proceed with the measurements. If it does not, repeat steps 1-4. If you still can not calibrate the electrode/meter, *stop* the analysis and check Appendix B for possible solutions or call the CAL for assistance.

Measure the QUALITY CONTROL CHECK SAMPLE

5. Remove the electrode from the 7.00 buffer and rinse it thoroughly. Gently blot the electrode tip. Measure the QUALITY CONTROL CHECK SAMPLE using the same conditioning rinse technique outlined in steps 2 and 3 above. Allow the system to stabilize until the readings differ by no more than +/- 0.01 pH unit within a 30 second period, but wait no more than 10 minutes. Record the reading in the space marked CHECK SAMPLE. The check sample should read 4.30 +/- 0.10 pH unit. If your measurement is outside of this range contact the CAL for assistance. *Continue* with the measurement of the PRECIPITATION SAMPLE pH.

Measure the PRECIPITATION SAMPLE

6. Rinse the electrode thoroughly with deionized or distilled water. Gently blot the electrode tip. Fill a clean vial from the syringe which contains the precipitation sample aliquot. Insert the electrode into the vial and allow it to remain there for 30 seconds. Remove the electrode, dump the conditioning rinse, refill the vial and reinsert the electrode directly into the refilled vial. Allow the system to stabilize as described in the previous step.[4] Record the measured pH value in the space marked PRECIPITATION SAMPLE.

Store the pH Electrode

7. Discard any remaining sample or standard aliquots and any used sample vials. Rinse the electrode thoroughly with deionized or distilled water one last time. Blot the tip with a clean absorbent laboratory wipe. To store the pH electrode either wrap the tip in Parafilm or allow it to hang uncovered in the air [5]. Replace the fill hole plug, taping it on if necessary, to prevent excess crystal growth.

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[4] Samples collected in western regions typically have measured values above pH 5.00 and extremely low H^+ ion activity making them more difficult to measure. Additionally, these sites are often located in semi-arid regions where there is less rainfall and hence fewer field chemistry measurements being made. Western sites experiencing sample stability difficulties should be aware that both of these conditions may result in longer stabilization times *for real precipitation samples*. Up to 10 minutes may be required.

[5] *DRY* electrode storage between readings is specific to the type of Beckman electrode supplied by the NADP/NTN program. Manufacturers of other brands of electrodes may suggest other methods.

3.3.5. Remarks/Supplies

SUPPLIES Block 10:

The CAL will supply upon request *only* those items listed in block 10. The supplies will be sent with one of the clean buckets returned to the site. Continue to circle the desired item on each field form you submit until the item is received. A 'supplies enclosed' sticker will appear on the box to alert you that something additional is enclosed. Please check EACH incoming black mailer as soon as it is received for requested supplies and important notices. Other supplies and equipment replacement parts are the responsibility of each individual site.

REMARKS Block 11:

The REMARKS space is used to record any equipment failures, repairs or calibration, unusual problems, events, weather, contamination or other occurrences at the field site or field laboratory. Unusual occurrences in the site area could include plowing, harvesting, burning, increased atmospheric pollution or dust, power outage, etc. *The importance of the information requested in the remarks section cannot be overemphasized.* Careful observation of the sample and occurrences in the surrounding environment can aid greatly in evaluating the validity of the sample and in the interpretation of the data collected. Use extra paper if necessary to document these occurrences.

3.4. Mailing Instructions

Secure the lid to the bucket(s) by hammering in place with a rubber mallet as follows:

1. Place the bucket and lid on a hard floor surface.
2. Place your free hand on the center circle of the lid and press down.
3. With your rubber mallet, hit down on the outside edge of the lid. Note that there are mold scars on the perimeter of the lid which mark the fasteners. Try to hammer on these points. Hit the bucket starting at the 12 O'clock position and work your way around the edge rather than hitting on one side and then another.
4. After the lid appears to be on the bucket, test the seal by running your finger around the perimeter of the lid, feeling for any gap between the lid and bucket.

All sample buckets regardless of their type (WET or DRY) should have a lid secured to the bucket. For WET-SIDE samples, sample leakage during shipment has been a common problem. For DRY-SIDE samples or dry WET-SIDE samples, the lid prevents contaminants such as the horse-hair packing from entering the bucket.

5. Place the sample container into a plastic bag removed from the new bucket or lid and seal tightly with the twist tie.
6. Enclose the white and yellow copies of the completed FIELD OBSERVER REPORT FORM and the original RAIN GAGE CHART in the shipping box along with the sample bucket and ship to the Central Analytical Laboratory. The pink copy is for your site records. When shipping the bucket be sure the pre-addressed mailing card on the shipping box has the correct address showing.

Buckets should be sent no later than two days after the sample has been removed from the field.

4.0. Preliminary Data Printouts

Once per month information made available to the CAL via the Field Observer Report Form (FORF) and preliminary results of the CAL's chemical analyses on each site's submitted samples are returned to the site's operator and supervisor in a two page computerized reporting format. The report additionally contains computer-generated messages which alert the site operator and supervisor of any inconsistencies that were noted in the data during the initial quality assurance evaluation steps performed at the CAL.

The first reports are received approximately 6 weeks after a site begins operation and monthly thereafter. Site operators and their supervisor are expected to review these two reports and respond to all of the computer generated messages. It is also requested that any other information regarding data quality that results from this review be forwarded to the CAL. Responses are made by annotating the appropriate report and mailing it back to the CAL in the black, bucket shipping container during the *next regularly scheduled* sample submission.

4.1. CAL Field Printout

The Field Printout is designed to provide the site operator and supervisor with the the Field Observer Report Form information the Network will use in its subsequent evaluation of the site's weekly data. It also includes collaborating information generated by the NADP/NTN monitoring program (i.e. laboratory pH and conductance values, precipitation volumes and evidence of sample leakage) and notes and error messages that alert the operator and supervisor to potential problems with the information furnished. These notes are based upon checks future data users are likely to make in order to determine if NADP/NTN operating protocols were followed. A key to the report follows along with a listing of the notes and error messages now in use.

Printout Date

The DATE in the upper left-hand corner of the computer sheet indicates when the printout was generated.

Sample ID

The SAMPLE ID is 12 characters in length and is assigned at the CAL to identify each sample. The first letter 'N', identifies the NADP/NTN project. Characters in positions 2 through 6 indicate the CAL sequential number for the project. The 7th character is used to identify such things as samples which are split at the CAL and samples which are reanalyzed. This letter should normally be an 'O' which identifies an ordinary sample. The 8th character is a 'W' for samples from the wet-side of the collector or a 'D' for samples from the dry-side of the collector. The characters in positions 9 through 12 identify the state and the number of the site within that state.

Lab Type

The LAB TYPE is a code assigned by the CAL which indicates the amount of liquid contained in a sample when it arrived at the CAL and the type of handling the sample will receive prior to analysis. The first letter (i.e. T, W or D) indicates the amount of liquid observed when the CAL removed the lid from the sample bucket as it arrived from the field. The second letter (i.e. A or B) indicates the amount of dilution water added to the sample when dilution is necessary to provide an adequate sample for a complete chemical analysis. Codes currently used are as follows:

T	Used only for buckets from the wet-side of the field sampler. It indicates a trace of water was in the bucket such that pH and possibly conductivity were measured for the sample. No additional chemical parameters were determined.
W	Indicates that a wet-side bucket arrived at the CAL with about $35mL$ or more of water. Chemical analyses were performed without any need for dilution.
WA	Indicates that the sample bucket arrived with less than about $35mL$ of water. $50mL$ of dilution water was added to provide an adequate sample for the anion-cation analysis. WA currently is a LAB TYPE used only for samples originating from the wet-side of the field sampler.
DA	Indicates that no water was visible in the wet-side bucket when it arrived at the CAL and that $50mL$ of dilution water was added to dissolve and analyze for contaminates.

For those sites submitting dry-side buckets two additional Lab Types are used to report dry-side data.

DB	Indicates that the dry-side bucket arrived at the CAL with no water in it and that $250mL$ of water was added to dissolve the deposited matter for analysis. Dry-side samples would never contain water if the field collector functioned perfectly.
WB	Indicates that the dry-side bucket arrived from the field with water in it. $250mL$ of water is added to these samples for dilution, regardless of the water already present.

Date On/ Time On

DATE ON/ TIME ON and DATE OFF/ TIME OFF identify the time period over which the sample was collected. For consistency, times are reported as Local Standard Time (LST).

pH/ Lab Fld

These are the pH measurements made by both the CAL (LAB) and the NADP/NTN operator (FLD).

Conductivity/ Lab Fld

These are the conductance measurements made by both the CAL (LAB) and the NADP/NTN operator (FLD).

Sample Volume

SAMPLE VOLUME is the difference between the final weight measured by the site observer and the bucket plus lid weight summed at the site and checked at the CAL. As such it represents the water volume in the bucket when it was removed from the collector. For a DRY-SIDE bucket, a large SAMPLE VOLUME indicates a sampler malfunction. For samples having a LAB TYPE of DA, sample volumes will be recorded as $0mLs$.

Sample Depth

SAMPLE DEPTH is the equivalent rain gage depth of the SAMPLE VOLUME.

Precip Depth

PRECIP DEPTH is the weekly value of precipitation from the Belfort rain gage.

Leakage

LEAKAGE signifies the amount of sample observed in the plastic bag encasing the bucket when the bucket shipping container was opened at the CAL. Leakage is classified into 4 categories: NONE; Trace-$10mL$ -TINY; 10-$100mL$ - SOME; and $> 100mL$ -LOTS.

Notes and Error Messages

Error 1. Time (Date) on for sample ______ precedes the time (Date) off for sample ______. Please notify CAL of the correct times (Dates) by sending a note with your next bucket mailing.

Note 2. Time between sample ______ off and sample ______ on is more than 59 minutes (# of hours given). Possible missing samples.

Note 3. The sample interval for _______ was nonstandard. The interval was _______ days.

Note 4. _______ did not have a standard Tue-Tue sampling period. Actual sampling period was Mon-Mon (or the like).

Note 5. The field pH for sample _______ (pH) was outside the expected range for precipitation samples. (Expected range is 3.0 to 9.0.)

Note 6. The lab pH differed by more than 1.0 pH unit from the field pH for sample _______.

Note 7. The field conductivity for sample _______ was outside the expected range for precipitation samples (expected range is 1.0 to 300.0).

Note 8. The lab conductivity differed by more than 20 μmho from the field conductivity for sample _______.

Note 9. The liquid depth of sample _______ does not compare well with the precipitation depth recorded for that period. If you have not done so, please send CAL any information you have that might explain the difference.

Note 10. Sample _______ had major leakage during shipment to CAL.

Note 11. A required date or time for sample _______ is missing. Please notify CAL of missing information by sending a note with your next bucket mailing.

Note 12. Sample _______ was not bagged. Please bag all buckets before shipment to CAL.

Note 14. Sample _______ did not have the lid pounded onto the bucket. Please be sure to pound the lid on all buckets sent to CAL.

Note 15. At the CAL it was noticed that the lid was not completely secured to the bucket for sample _______ . Please be sure to pound the lid on all buckets sent to CAL.

Note 16. Standards for the collection and on-site handling for sample _______ were not satisfied, therefore data for this sample will be flagged non-standard.

4.2. CAL Preliminary Printout

The atmospheric deposition data provided monthly by the CAL to each active NADP/NTN site is always to be considered preliminary. Measured values reported to the sites are still undergoing quality assurance evaluations and in some cases may be reanalyzed as a part of this process. Additionally, data integrity checks and the evaluation of the field information submitted with each sample may identify deficiencies in sampling protocol which could result in the flagging and/ or subsequent sequestering of these values from the finalized NADP/NTN data base. A key to the report follows:

Date

Same as above section 4.1..

Sample ID

Same as above section 4.1..

Lab Type

Same as above section 4.1..

Date On/ Time On

Same as above section 4.1..

Concentrations

The ion CONCENTRATIONS on the computer printout for wet-side samples with a LAB TYPE of 'W' or 'WA' represent the values for the sample as it arrived at the CAL. That is, the CAL has made the mathematical correction for any dilution water added. For wet-side samples with a LAB TYPE of 'DA', the ion concentrations are the values in the dilution water itself.

The ion CONCENTRATIONS for the dry-side samples are the values measured in the dilution water ***plus*** any water originally present in the bucket when it arrived at the CAL.

All measured concentrations that are at or below the analytical detection limit are reported with a less than symbol of '<' (e.g. < .003 mg/L). The detection limit values are reported either as raw measurements or as raw measurements corrected for the added dilution water depending on the standard procedure outlined above for each wet or dry side sample and LAB TYPE.

Field Cond/ Field pH

FIELD COND and FIELD pH are measurements of sample conductance and pH made by the NADP/NTN operator.

Lab Cond/ Lab pH

LAB COND and LAB pH are measurements of sample conductance and pH made at the CAL.

Deposition

The deposition values for wet-side samples of LAB TYPE 'W' or 'WA' are calculated using the SAMPLE VOL (see below) and CONCENTRATION measurements. For dry-side samples the volume used is that of the dilution water plus any water that may have been in the bucket upon arrival at the CAL. If the CONCENTRATION is a detection limit measurement, the DEPOSITION is calculated using the detection limit value and the result is reported as a detection limit value.

Deposition values are not calculated for other LAB TYPES.

Sample Vol

SAMPLE VOL is the difference between the final weight measured by the site observer and the bucket plus lid weight summed at the site and checked at the CAL. As such it represents the water volume in the bucket when it was removed from the collector. For a dry-side bucket, a large SAMPLE VOL indicates a sampler malfunction. For samples having a LAB TYPE of DA, SAMPLE VOL will be recorded as $0 mLs$.

Meas. Anions/ Meas. Cations

The MEAS ANIONS/ MEAS CATIONS columns are the respective sums of the measured anion and cation concentrations converted to units of microequivalents per liter. The conversion factors used by NADP/NTN for changing mg/L to μequiv$/L$ are included below. For the ions listed, multiply the given factor by the CONCENTRATION for the respective ion in mg/L to obtain concentrations in μequiv$/L$

Anions		Cations	
$SO_4^{=}$	20.83	NH_4^+	55.44
NO_3^-	16.13	Ca^{++}	49.90
Cl^-	28.21	Mg^{++}	82.26
$PO_4^{\equiv}$	31.59	K^+	25.57
		Na^+	43.50

Hydrogen ion is also included in the cation sum on the printout and can be calculated in units of μequiv$/L$ by evaluating:

$$(10^{-LABpH}) * (10^{6})$$

5.0. Special Maintenance of Field Equipment

Routine maintenance directions for both the Aerochem Metrics Precipitation Collector and the Belfort Recording Rain Gage are given in section 5 of Appendices C and D. Please consult these sections of the manual for these procedures.

5.1 Aerochem Metrics 301 Wet/Dry Precipitation Sampler (see also Appendix C)

5.1.1. Sensor Heater Check

Each week, test the precipitation sensor to confirm that the sensor heater is fully operational and that the Wet/Dry Collector responds to the wet and dry sensor. The check is made with the following test.

1. Check the temperature of the sensor on the Aerochem Metrics collector by pressing a finger against the *sensor plate.* It should be cool unless the collector has been open within the last several minutes.
2. 'Short out' the *sensor grid* with water. DO NOT USE METAL TO SHORT THE GRID. Apply enough water to ensure that the collector stays open for 5-10 minutes.
3. Allow the lid mechanism to move over and cover the DRY-SIDE bucket. Observe the movement of the lid. It should operate freely with little motor noise and rest snugly over the bucket.
4. Walk over to the recording rain gage and while the collector is open (the WET-SIDE bucket is exposed) check to make sure the *event recorder pen* is up. The up position indicates the correct operation of the motor box.
5. After the collector has been open for 5-10 minutes, check to make sure the *sensor plate* is warm.
6. Blow any remaining water off the sensor and observe the lid movement as it covers the WET-SIDE bucket. The lid should move smoothly and complete its cycle in approximately 5 seconds.

5.1.2. Sensor Head Cleaning

Periodically wash the rain sensor grid with clean water to remove any accumulation of minerals, bird droppings, etc., that could close the circuit and cause a false event circuit. Such a short leaves the wet-side bucket exposed during dry periods. The sensor can be scrubbed with a toothbrush soaked with deionized water or alcohol. Alternately, the sensor can be cleared of debris by cutting a strip of Manilla from a file folder or card to a width of 45*mm* and passing the strip under the grid and between the Teflon washers that fix the separation of the grid and plate.

5.1.3. Foam Lid Seal Cleaning and Replacement

Every eight weeks (if temperature permits) the polyethylene underside and top section of the Aerochem Metrics collector's lid should be cleaned with distilled or deionized water and wiped with a clean laboratory tissue. This removes loose dirt on the lid surfaces and limits any excess build up of contaminants. The CAL sends a reminder of this maintenance procedure to all sites every eight weeks via the U.S. mail.

Approximately every 18 months the CAL will send a new foam lid seal to each site along with instructions for its installation. This replacement further limits contamination and helps ensure a tight bucket seal.

5.1.4. Winter Operation

Depending on the geographic location of the site, winter operation may or may not pose a serious problem for collecting wet and dry deposition. The two most common problems encountered during winter operation of the Aerochem Metrics sampler are the freezing of the collector lid to one of the buckets and the immobilization of the lid due to heavy snow or ice accumulation. Typical symptoms of the above problems include: rain gage indicates more precipitation than is accounted for by the bucket volume, and event recorder does not indicate the correct number of events; event recorder indicates bucket stayed open for unusually long periods after precipitation event; snow and ice in the DRY-SIDE bucket; repeatedly blown fuses; worn thrust collars and burned out motor.

If any of these problems are regular occurrences at your site then the investment in a peaked snow roof and/or heated pad should be made. These are available through Aerochem Metrics. Once installed they remain on the collector through all seasons as a permanent modification. *Under no circumstances should the foam seal be removed to alleviate these problems.* Consult with the CAL concerning this or any other collector modification.

5.2. Belfort 5-780 Recording Rain Gage (See also Appendix D)

5.2.1. Winter Operation

Blowing snow poses the biggest problem in the winter operation of the rain gage. Besides the inaccurate measurement of precipitation caused by snow blowing out of the gage, the dash pot may be damaged if snow finds its way into the weighing mechanism. To prevent both of these problems the network requires sites to 'winterize' their rain gages with the following procedure. Sites not completing the procedure may have snow or mixed precipitation amounts invalidated.

The CAL will notify sites once each winter of the winterization procedure. The notice serves as a reminder of the importance of the winterization. The notice may come too early for some sites and too late for others. Sites in northern regions should not wait for the memo ! Each site is responsible for implementing the winterization at the appropriate time for their site.

Winterization Instructions

A. Remove the funnel that is fixed to the bottom of the top cap by rotating the funnel until its bead clears the pins in the collector tube. Then lift it off.

B. Empty the catch bucket, replace it in the gage, and add standard automotive antifreeze to it until the gage reads an equivalent of 2 ¾ *inches* of precipitation.

C. Do not make any zeroing adjustment to the gage after adding the antifreeze to the bucket.

D. Stir the antifreeze solution in the bucket each week after moving the recording pens away from the rain gage chart drum.

Table 5 gives the approximate freezing temperatures of the antifreeze solution when diluted by additional water-content to the equivalent rain gage reading indicated. The catch bucket should be emptied and recharged with fresh antifreeze whenever the gage level and the prevailing temperatures indicate that freezing of catch is probable.

Table 5. Gage Catch Freezing Temperature

Gage Reading, Inches	5	6.5	7.5	12
Freezing Temperature, °C	-37	-24	-18	-9

5.2.2. Calibration Checks

Without a 'linearity tool' and a set of calibration weights available through Belfort Instrument Co., only calibration checks may be made. Calibration should be checked at least twice per year and any time consistent disagreement between the rain gage and Aerochem Metrics sampler cannot be explained. Be sure to report the results of this check in the REMARKS block on the FIELD OBSERVER REPORT FORM.

Should recalibration become necessary a properly equipped, qualified person should be contacted to recalibrate the instrument. Factory recalibration is available through Belfort Instruments.

Calibration of the gage is based on the assumption that 822.7*grams* of water in the 5-780 series gage equals 1*inch* of precipitation. The check is best made at mid-range, which, for this gage is at 3*inches*. To check the calibration, zero the gage with a dry rain gage catch bucket in place. Add 2468*grams* of water to the dry bucket. The chart should indicate 2.90-3.10*inches* of precipitation.

A second check that can be made periodically verifies the turnover point of the dual traverse gage. The check is made by gently pushing down on the bucket until the two pens pass each other near the top of the chart and the rain gage pen begins to reverse direction. The precipitation pen should pass freely under the event recorder pen and reverse directions exactly at the 6 inch horizontal calibration line. In addition, the rain gage trace should parallel the vertical time lines. Deficiencies should be reported promptly to the CAL.

A final check tests the sensitivity of the gage to precipitation events. This check involves gently tapping the inside of the bucket with your finger and observing the precipitation pen. A quick 'nervous' response from the pen should be observed with very little effort being applied to the bucket.

6.0 Quality Assurance Programs

Periodically, monitoring sites will be required to participate in various NADP/NTN external Quality Assurance Programs. These programs, which are administered by the U.S. Geological Survey (USGS) and the U.S. Environmental Protection Agency (EPA), are designed to document the quality of work performed at each field laboratory and at the Central Analytical Laboratory (CAL), and to evaluate the representativeness of the samples submitted by each monitoring station. An explanation of each of the external programs is presented below. Results of the Intersite Comparison and Blind Audit program are published in U.S. Geological Survey Water-Resources Investigations Reports (available through the U.S. Geological Survey, Denver, CO 80225). Results of the Site Visitation Program are published in NADP/NTN Quality Assurance Reports.

6.1. The NADP/NTN Intersite Comparison Study

Semi-annually an aliquot of a standard solution prepared by the U.S. Geological Survey is sent to each site to be evaluated for pH and specific conductance. Each site operator is asked to analyze the aliquot and return the unused portion in its original container to the USGS within 45 days. The solutions are submitted as unknowns to the operators. Specific procedures for each Intersite Comparison are described in information sent with each sample. Results are tabulated and compared by USGS to values measured by USGS and other NADP/NTN sites. Results are also reported back to each site operator.

6.2. The NADP/NTN Blind Sample Program

The Blind Audit Program requires each site to submit a quality assurance sample, blind to the Central Analytical Laboratory, approximately once every two years. On a specified schedule, a site submits an extra sample in a clean bucket to the CAL as if it were a real precipitation sample. A portion of the sample is submitted directly to the CAL. Both portions are analyzed thereby allowing an overall check of the level of contamination that may have resulted from the field handling, laboratory handling and the storage and transportation protocols of the NADP/NTN sampling program. The program submits 2 samples per week to the CAL.

Participants in the program are sent specific instructions with each Blind Audit sample. In addition sites are contacted by telephone approximately one week prior to the Blind Audit submission to verify the receipt of the Blind Audit sample and to discuss any problems or questions operators may have concerning the submission.

6.3. The NADP/NTN Site Visitation Program

Under the NADP/NTN Site Visitation Program, monitoring sites are visited once every three years. During this 'visit' sites are inspected and photographed to document the representativeness of the station as a regional, background location for measuring atmospheric deposition. Siting deficiencies and equipment malfunctions are noted and remedial action is suggested. In addition to the inspection, field sample handling techniques, laboratory techniques and site documentation are audited to determine if NADP/NTN protocols are being followed and to suggest improvements in technique which might prevent the loss of information or samples in the program. The visiting NADP/NTN inspector may also assist the operator in making minor adjustments to sampling equipment. Operators are encouraged to ask questions and express any concerns about the program.

Site operators and supervisors are notified approximately 1 month in advance of planned site visits. The visits should occur during a mutually agreed upon time when both the site operator and supervisor are available. Visits usually require 4 to 5 hours.

7.0 Directory

7.1. National Atmospheric Deposition Program

Program Coordination Office
Natural Resource Ecology Laboratory
Colorado State University
Fort Collins, Colorado 80523

J. H. Gibson, (303) 491-1978
Program Coordinator

Carol Simmons, (303) 491-1989
.. siting and installation questions

Linda Bandhauer, (303) 491-1977
.. general program information
.. contracts and billings
.. published reports
.. training courses

Gwen Scott, (303) 491-1465
.. data requests
.. data tapes

Dave Bigelow, (303) 491-5574
.. quality assurance

Central Analytical Laboratory
Illinois State Water Survey
2204 Griffith Drive
Champaign, Illinois 61820

Gary Stensland, (217) 333-2213
Director, Central Analytical Laboratory

Scott Dossett, (217) 333-0249
.. CAL computer printouts
.. sampling equipment questions

Jackie Saur, (217) 333-3936
.. shipping and supply problems
.. field measurements

Mark Peden, (217) 333-8325
.. general questions about analytical procedures

7.2. External Quality Assurance Programs

U.S. Geological Survey
Box 25046, MS 408
Denver Federal Center
Denver, Colorado 80225
(303) 236-3605

LeRoy J. Schroder
.. Intersite Comparison
.. Interlaboratory Comparison
.. Blind Audit Program

Center For Environmental Measurements
Research Triangle Institute
Box 12194
Research Triangle Park, NC 27709
(919) 541-6720

W. Cary Eaton
.. Site Visitation Program

7.3. Instrument Manufacturers

Aerochem Metrics, Inc.
Route 2, Box 112
Bushnell, Florida 33513
(904) 793-8000

Belfort Instrument Company
727 South Wolfe Street
Baltimore, Maryland 21231
(301) 342-2626

Appendix A
NADP/NTN Equipment Requirements

Appendix A NADP/NTN Equipment Requirements

Wet/Dry Precipitation Collector

The Aerochem Metrics Model 301 Automatic Sensing Wet/Dry Precipitation Collector is the only collector meeting the NADP/NTN monitoring network requirements.

Recording Rain Gage Equipped with an Event Recorder

The Belfort Universal Rain gage, model 5-780 equipped with an Aerochem Metrics Event Recorder is the only Rain Gage/ Event Recorder combination meeting the NADP/NTN monitoring network requirements.

> NOTE: Products listed below are examples of equipment meeting the requirements of the project. Listing of these products does not constitute endorsement by the project staff. Listed items may vary considerably in their cost, serviceability and in the level of of expertise required to properly use the item. Starred (**) items are those currently being used by the CAL laboratory staff.

Balances

Requirements: 20*kg* capacity and 1*gm* sensitivity

Example:

**1. Ohaus model 1119D

Specific Conductance Meters

Requirements: 0.1-1,000 $\mu S/cm$ range and readability to 0.1 $\mu S/cm$

Examples:

**1. Yellow Springs Instrument, Model 32

**2. Yellow Springs Instrument, Model 31

**3. Yellow Springs Instrument, Model 35

4. Yellow Springs Instrument, Model 34

5. Markson, TU-4603 - solution analyzer for both pH and specific conductance

Portable Models

**1. Barnstead Model PM-70 CB

**2. Altex RC-16C

3. Yellow Springs Instrument, Model 34

4. Lab-Line Lectro Mho meter, Mark V

Specific Conductance Electrodes

Requirements: Cell constant of 1.0 and a sample volume requirement of $< 10ml$.

Examples:

**1. Yellow Springs Instrument Model 3403 (dip or fill)
**2 Yellow Springs Instrument Model 3417 (dip or fill)
**3. Markson, TU-30515 (dip)
4. Barnstead Model E3416 (dip)
5. Lab-Line Model 11201 (beaker)

pH Meters

Requirements: Read 0-14 pH units, digital display with readability to 0.01 pH units, separate calibration, slope, and temperature controls.

Examples:

1. Altex/Beckman - Models **3500, **3560, **pHI71, **pHI21, pHI31
2. Corning - Models 120, 140, 145, 150, 155
3. Orion - Models 501, **601, 611, 701, 811, 901
4. Fisher - Models 805MP, 815MP

pH Electrodes

Requirements: Refillable glass combination electrode with an annular ceramic junction

Examples:

Beckman Refillable, Epoxy Body, Futura II, Combination Electrode, Model 39835 (34104-980) with 36*in* Keeper Cable is currently supplied by the CAL. A second back-up electrode of the same type should be available at the site. The Program does not supply backup equipment.

Beckman products are available only through Beckman Scientific Instruments or VWR Scientific.

Suggested Labware

1-250*ml* wash bottle
Laboratory wipes such as Kimwipes
Distilled or deionized water, conductivity below 2 $\mu S/cm$
Parafilm
Rubber Mallet

Appendix B
Troubleshooting pH and Conductivity Measurements

Appendix B Troubleshooting pH and Conductivity Measurements

Introduction

This Appendix is intended to assist field personnel in diagnosing problems with pH meters and electrodes, and conductivity meters and cells. There are far too many makes and models of equipment to discuss them individually, but the basic principle of operation is similar. A discussion of the theory of pH measurements, and the operation of pH electrodes and conductivity cells is presented. It is strongly recommended that all field personnel have an owner's manual and become familiar with the operation and maintenance of their own particular meter, electrode, and cell. Manuals can be obtained from the appropriate manufacturer. Spare pH electrodes should be available at each field site.

pH Measurements

There are many problems that may occur when measuring the pH of precipitation samples. Most are due to the low ionic strength of the precipitation samples being measured. Rarely is the pH meter at fault. Meter checks however, are often the easiest to perform and are therefore given first. If the ionic strength of the sample is not the cause of the problem, the next most likely source is the solutions used, followed by the condition of the pH electrode. Solutions and electrodes are usually checked first as they are the most likely causes of measurement problems.

Troubleshooting

If problems occur in calibrating your pH instrumentation or when measuring the pH of a precipitation sample, it is best to contact someone at the CAL (consult the directory in section 7.0). If you wish to try a few simple diagnostic procedures the following steps are offered:

Electrical Connections

1. Disconnect and reconnect the cable from the meter.
2. Disconnect and reconnect the cable from the electrode, being careful not to overtighten the connection.
3. If the meter is battery operated, a weak or dead battery is a likely cause of the problem. Consult the owner's manual for directions on checking the battery and the meter performance in general. Some older meters are AC powered but use a mercury battery for the reference potential. These batteries should be tested under load, that is with the meter turned on, and should be replaced when they have dropped to 10-15% below their rated voltages. If the batteries are not at fault, check the owner's manual for specific troubleshooting tests before contacting the CAL or the site supervisor for assistance. In many cases the only option will be to return the failing meter to the manufacturer for repairs.
4. The slope control or calibration dial provides a good indication of how the pH electrode and meter are functioning. Mark or record the position of the dial and note how far the dial has to be turned during calibration each time a calibration is performed. The fact that the dial has to be turned more and more each time, is an early indication of problems with the pH electrode or meter.

Electrode Problems

The pH electrode is especially important to obtaining accurate measurements. Most problems attributable to pH equipment are associated with a faulty electrode. In an attempt to minimize these problems the NADP/NTN network began supplying field sites with a pre-tested single type of pH electrode. The CAL staff are available to assist in solving problems when they occur and provide replacement electrodes. If you wish to try a few more simple diagnostic procedures the following steps are offered;

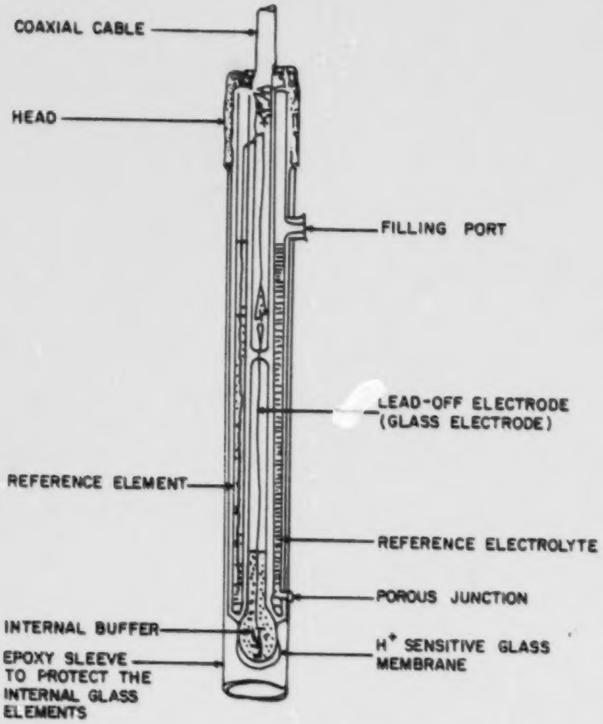
5. Empty the electrode of filling solution. This is accomplished by holding the black section of the electrode near the filling port and shaking out the solution inside. Refill the electrode with new filling solution and recheck electrode preformance.
6. If crystals are present inside the electrode, empty the electrode as described above. Rinse the inside of the electrode and fill it with deionized or distilled water. Leave the electrode overnight in a beaker of deionized or distilled water. The next morning remove the water and rinse the electrode 2-3 times with filling solution. Refill the electrode with fresh filling solution and recheck electrode performance.
7. If performance is still not satisfactory then call the CAL.

Theory of Operation

Shown in Figure B-1 is a cross section of a typical combination pH electrode. The bulb at the tip is a special conductive glass that is sensitive to hydrogen ion activity. This bulb is sealed onto a non-conductive glass tube which is filled with a buffered electrolyte whose pH value and ion concentration are fixed. Surrounding the glass electrode is the reference electrode. This electrode provides a stable reference potential and completes the electrical measuring circuit. The silver/silver chloride element of the reference electrode is immersed in an electrolyte filling solution thereby producing a constant voltage. This design ensures that stable potentials are developed on both the internal reference element and the inner surface of the glass bulb. When electrolyte from inside of the electrode passes through a porous junction to the solution being measured, an electrical charge is carried into the solution being measured. This results in a potential developing on the outer surface of the bulb. The difference between this potential and the constant internal one is the measure of the hydrogen ion activity of the sample. The pH meter displays the hydrogen ion activity as pH. The meter also contains controls which allow compensation for changes in temperature and the electrical circuitry unique to each electrode.

The free flow of electrolyte into the sample solution is a critical step in the measurement process. The electrode selected for use by NADP/NTN has an annular ceramic junction through which the electrolyte must pass. The annular design of the junction provides a large porous surface that has proven to be more resistant to clogging than other single point junctions. The formation of white crystals around the the bulb during storage means the electrode is functioning properly. These crystals are potassium chloride, the major compound in the filling solution. The crystals are easily soluble in water and should be completely removed in the rinsing steps of the pre-measurement procedure. The failure of these crystals to form when the electrode is stored in air is a good indication that the junction is clogged and measurements will be difficult if not impossible.

Figure B-1 Cross-Section of a Typical Combination Electrode


COAXIAL CABLE
HEAD
FILLING PORT
LEAD-OFF ELECTRODE (GLASS ELECTRODE)
REFERENCE ELEMENT
REFERENCE ELECTROLYTE
POROUS JUNCTION
INTERNAL BUFFER
H+ SENSITIVE GLASS MEMBRANE
EPOXY SLEEVE TO PROTECT THE INTERNAL GLASS ELEMENTS

New Electrode Activation

For new electrodes or electrodes that have been stored for extended periods of time, the following procedure is recommended;

1. Remove the tape from around the filling port, being careful not to lose the plug.
2. Next, before attempting to remove the cap, rinse the tip of the electrode with copious amounts of distilled or deionized water. This should dissolve any potassium chloride crystals that may have formed around the tip and will make it easier to remove the cap.
3. Add filling solution if needed and carefully shake the electrode as you would a fever thermometer to remove any bubbles that may have formed during shipment. Hold the electrode near the filling port by the black epoxy collar when shaking.
4. Connect the cable to the pH meter.
5. Condition the electrode by placing it into pH 7.00 buffer. Allow it to remain in the buffer for 24-48 hours. The filling port should remain open during this conditioning treatment.

6. Calibrate the pH meter/electrode assembly with pH 7.00 buffer and pH 4.00 buffer as directed in the measurements procedures of section 3.3.4. of this manual.
7. Measure the pH of the pH 4.30 check sample. The pH should be 4.30±0.10 within 10 minutes. Record the reading on the PERFORMANCE REPORT you received with your electrode and return the report to the CAL in the next black box you send.
8. If there is a problem contact the CAL.
9. Samples may be agitated slightly or carefully shaken to reach the expected pH range more rapidly, but it must be quiescent or stationary when the pH measurement is being taken.
10. Remember the filling port should be uncovered when measurements are being taken and covered when the electrode is being stored.
11. Studies at the CAL have shown that these electrodes typically reach stable readings in 3-5 minutes when the pH of the sample measures less than 5.5 and in 5-8 minutes when greater than pH 5.5. Please keep this in mind when measuring the pH of your sample. Never wait longer than 10 minutes.
12. Never report pH measurements when the electrode will not calibrate. Instead, note the problem on your FIELD OBSERVER REPORT FORM and contact the CAL.

Electrode Storage

1. When not in use, electrodes should be stored with the tip suspended in air or loosely wrapped with Parafilm. The filling port should be covered.
2. Always rinse the electrode with generous amounts of deionized or distilled water before use. This should dissolve any potassium chloride crystals that may have formed around the tip during storage.
3. If storage has been for approximately 1-4 weeks, simple rinsing with distilled or deionized water and replenishing of the filling solution should be all that is necessary before using the electrode.
4. If storage will be for longer than one month the electrode should be emptied of filling solution and stored completely dry. When needed, refill and leave overnight in buffer pH 7.00 with the filling port open.

Specific Conductance Measurements

Of the two chemical analyses that site operators perform, conductance is by far the easiest and least error prone. Most problems in conductivity measurements are due to measurement techniques or to the cell. Conductance readings are typically very stable over time, however, some slight drifting of the signal may occur due to the absorption of compounds (such as CO_2) from the air or from the electrolysis of the sample as the electrical current passes though the sample. The magnitude of the drift will also depend upon the scale sensitivity of the meter used. Should problems with conductance measurements arise the following procedures are recommended as a start at diagnosing the problem.

Conductance Meter

1. If the meter is battery powered, activate the meter's built-in power test function. Consult the owner's manual for specific details.

Conductance Cell

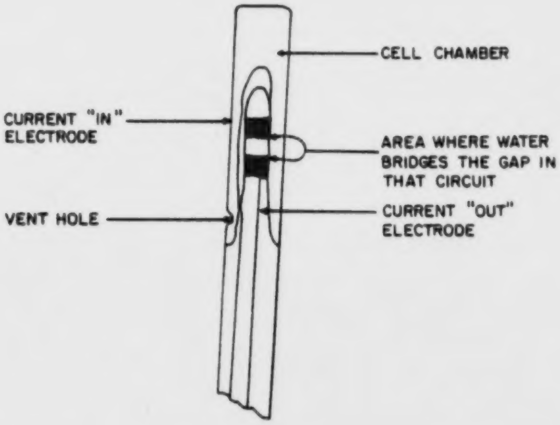
2. The single-most important requirement for accurate and reproducible results in conductivity measurements is a clean cell. The cell can be cleaned periodically in a warm detergent diluted with deionized water and rinsed thoroughly with deionized water.
3. The electrodes of the conductivity cell are either gold plated or are coated with platinum black. The platinum coated electrodes require frequent inspection to detect a thin or flaking coating. If this is observed the cell must be replaced.
4. If the above procedures do not restore the conductivity cell to satisfactory operation, contact the CAL. You will most likely need to replace the conductance cell. Please note however, that the NADP/NTN network does not supply sites with new conductivity cells.

Theory of Operation

Pure water is actually a poor conductor of electrical current. The conductivity measurement capitalizes upon this phenomena and is based upon the fact that the presence of ions such as H^+, HCO_3^-, $SO_4^{=}$, etc. changes the water's conducting properties. The platinum or gold coating that comprises the detection area of the cell is specifically designed to be highly conductive. The conductance meter supplies a voltage to one of the electrodes and then measures the drop in voltage at the other electrode. The difference in current between the two electrodes is proportional to the amount of ions in solution.

All conductivity cells provide a chamber at the end of their two electrodes. The most common cell is cylindrical (see below).

Figure B-2 Cross-Section of a Common Conductance Cell



The cell should contact the rain sample such that both electrodes are submerged and free of trapped air. This can be accomplished by slightly tilting the cell and gently tapping the side, or the cell can be moved up and down in the rain sample in a plunging motion. Some cells are designed to be used either in a 'dip' mode, where the entire cell is inserted into a beaker filled with the rain sample or in a 'fill' mode, where the sample is injected into the cell while the cell is inverted. The 'fill' method is highly desirable since it requires less sample volume for a measurement. In the dip mode the cell should never be allowed to come in contact with the sides or bottom of the beaker during the conductivity measurement. Additionally, if at all possible, the beaker containing the rain sample should be well insulated; i.e., not grounded since the presence of electrical fields and stray currents from stirrer motors, heaters, etc., can cause interferences during conductivity measurements. Equipment that is suspected of creating electrical fields should be disconnected during conductivity measurements.

Concluding Remarks

Field personnel should be encouraged to become as familiar as possible with the equipment by reading and occasionally reviewing the owner's manual. In the long run, familiarity with the owner's manual will save time and improve the quality of the measurement.

Appendix C
Aerochem Metrics Precipitation Collector Maintenance Manual

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1.0. INTRODUCTION

The Aerochem Metrics wet/dry collector is a fairly simple device which has proven to be reliable and efficient for capturing rainfall. This guide is intended to address troubleshooting and repair of the major collector components, namely the motor box, sensor, and clutch units. Site specific repairs such as battery checking, 110VAC power supply, and instrument mounting are not discussed. For information on these subjects see the NADP/NTN Instruction Manual for Site Selection and Installation.

IF YOU EXPERIENCE A COLLECTOR MALFUNCTION

(1) Please inform the CAL; call 217/333-0249, especially when replacement parts are needed or if sample quality has been affected.

(2) Briefly describe the malfunction and indicate when it first occurred on the Field Observer Report Form of the sample affected. Continue to do this for each weekly sample until the malfunction is eliminated. Pay particular attention to how the wet-side bucket was exposed. Recall that when the sampler is operating correctly, the wet-side bucket should only be open during rain, snow, etc.

Example: "Sensor heater went out on Thursday: wet-side bucket remains open for several hours after the rain stops."

2.0. PARTS REFERENCE LIST

This list identifies parts by name and assigns part numbers that are used in conjunction with the "Pictorial Guide to Parts" section which follows. Also, all part numbers are cross-referenced to a corresponding photo number.

Some part numbers are referenced in the "Trouble Shooting" section of this text; others are included so that this additional detail can be referenced in future communications. Individual part numbers are signified by parenthesis throughout the text (e.g. (1)=sensor unit).

Part name	Part No.	Photo No.
sensor unit	1	1
collector frame	2	1
sensor screws	3	1
sampling bucket holder	4	1
sensor grid	5	1
sensor plate	6	1
motor box screws	7	2 and 4
sampling bucket holder screws	8	2 and 3
motor box unit	9	3
clutch arm unit	10	3 and 6
clutch arm machine bolt	11	3
counterweight(s)	12	3
Waldes ring	13	3
push rod	14	3
counter weight rod	15	3
lid drive arms	16	3
lid tension springs	17	3
110v AC power cord	18	3 and 4
event recorder terminal	19	3 and 4
sensor unit socket	20	4
12V DC power lugs	21	4
12V DC circuit fuse	22	4
110V AC circuit fuse	23	4
event recorder circuit fuse	24	4
motor box stop switches	25	5
event recorder/wet mode heater switch	26	5
drive motor shaft	27	5
clutch tooth	28	6
thrust collar with set screw	29	6
clutch tooth tension plate	30	6
switching magnets	31	6
clutch tooth tension spring	32	6
silver drive arm	33	2

Components on Facing Page

Part Number	Name
1	sensor unit
2	collector frame
3	sensor screws
4	sample bucket holder
5	sensor grid
6	sensor plate

3.0. PICTORIAL GUIDE TO PARTS

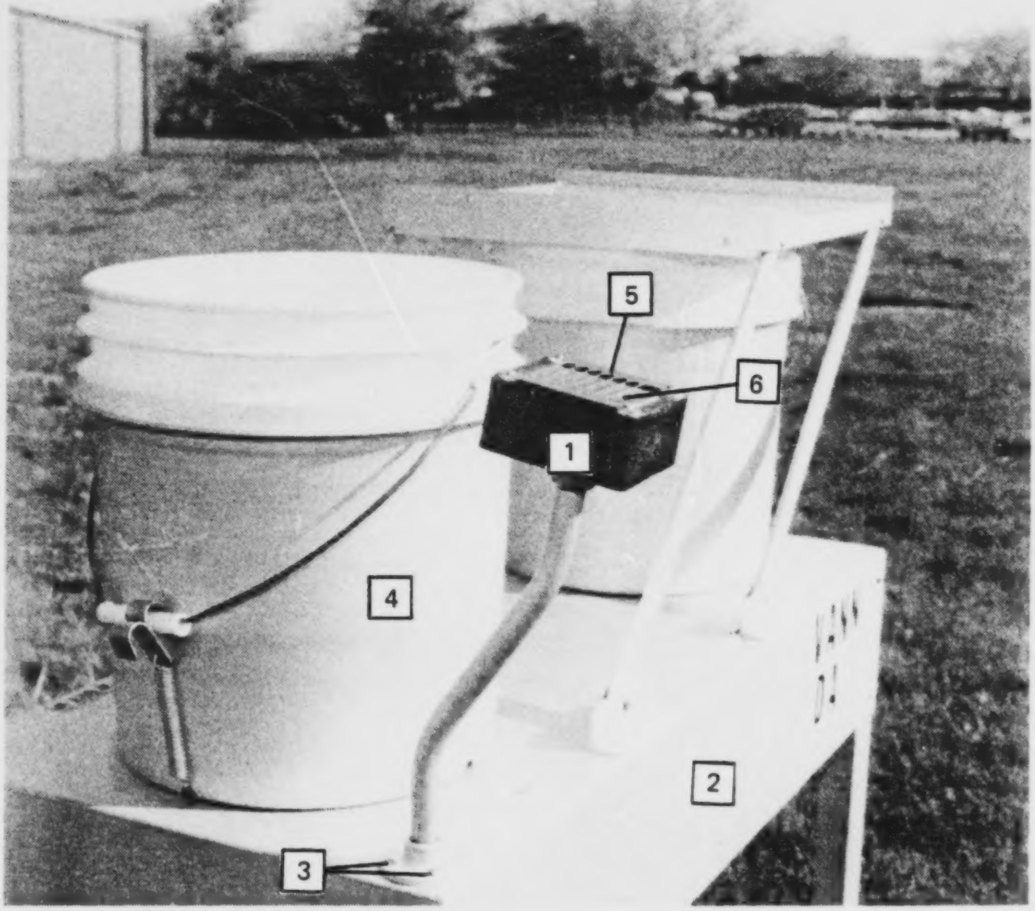


PHOTO #1
COLLECTOR MAINFRAME/ SENSOR

Components on Facing Page

Part Number	Name
7	motor box screws
8	sampling bucket holder screws
9	motor box unit
10	clutch arm unit
11	clutch arm machine bolt
12	counterweight(s)
13	Waldes ring
14	push rod
15	counter weight rod
16	lid drive arms
17	lid tension springs
18	110V AC power cord
19	event recorder terminal
20	sensor unit socket
33	silver drive arm

Reproduced from
best available copy.

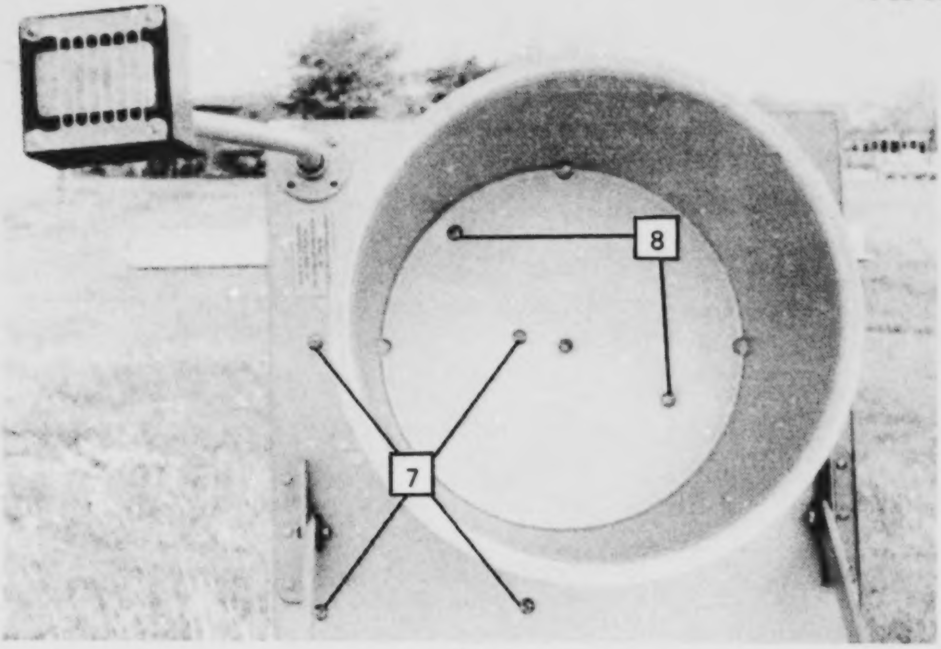
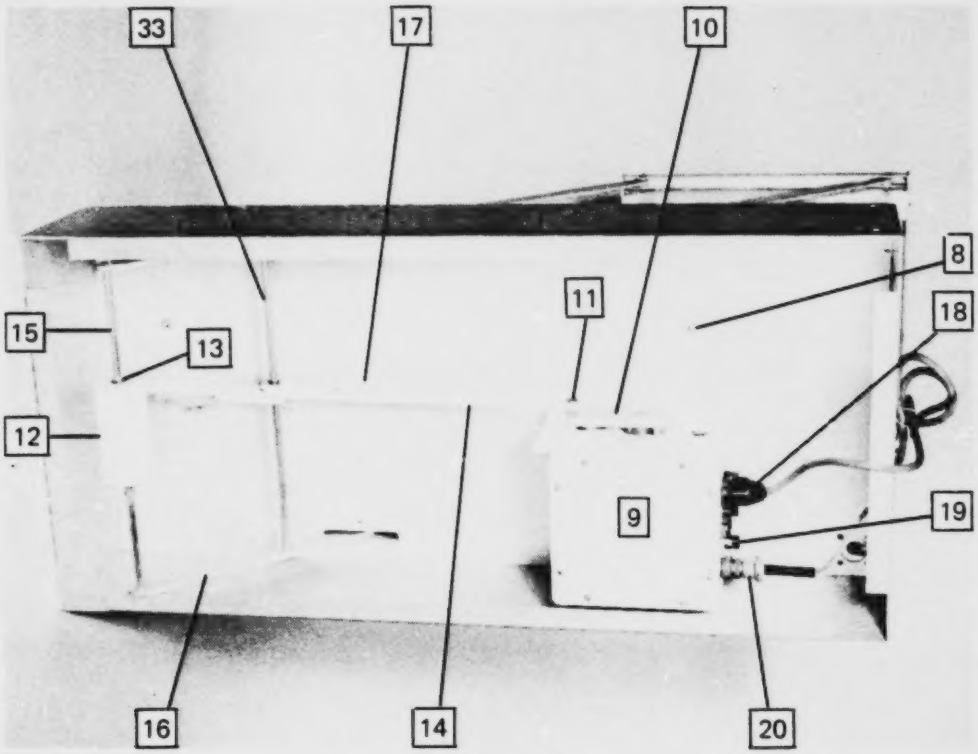


PHOTO #2
COLLECTOR MAINFRAME (TOP)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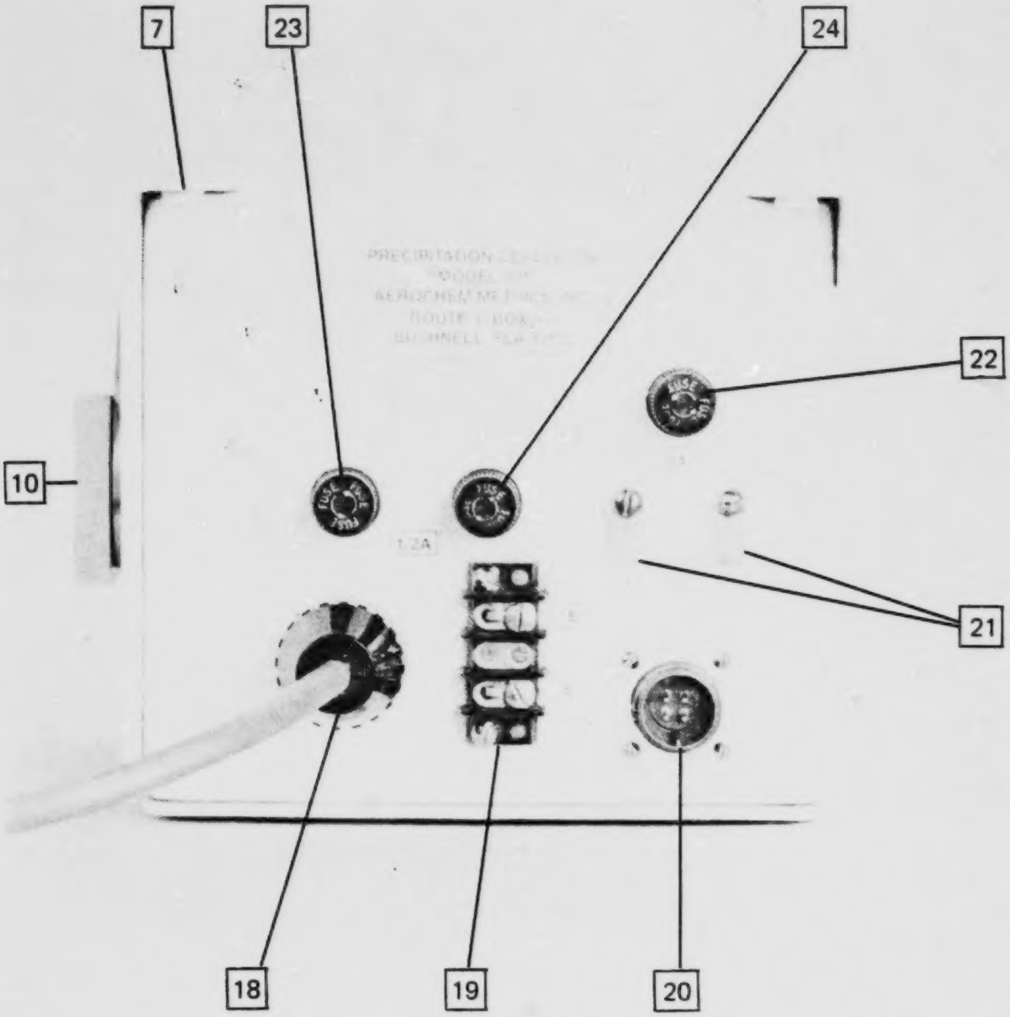
20

PHOTO #3
COLLECTOR MAINFRAME (UNDERSIDE)

Components on Facing Page

Part Number	Name
7	motor box screws
10	clutch arm unit
18	110V AC power cord
19	event recorder terminal
20	sensor unit socket
21	12V DC power lugs
22	12V DC circuit fuse
23	110V AC circuit fuse
24	event recorder circuit fuse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24
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1.2A
21
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19
20

PHOTO #4
MOTOR BOX (FRONT)

Components on Facing Page

Part Number	Name
25	motor box stop switches
26	event recorder/wet mode heater switch
27	drive motor shaft
28	clutch tooth
29	thrust collar with set screw
30	clutch tooth tension plate
31	switching magnets
32	clutch tooth tension spring

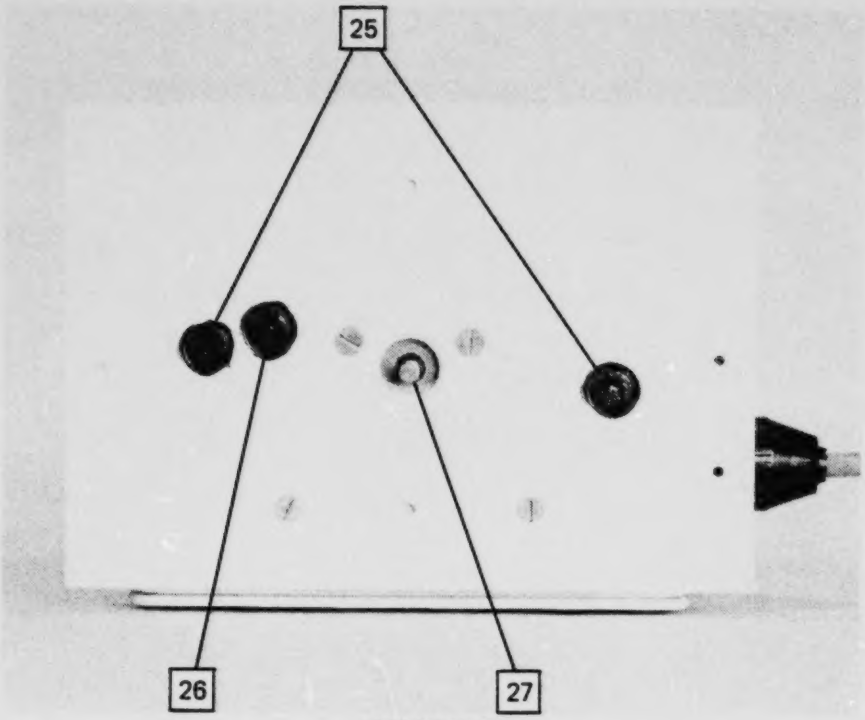


PHOTO #5
MOTOR BOX (SIDE)

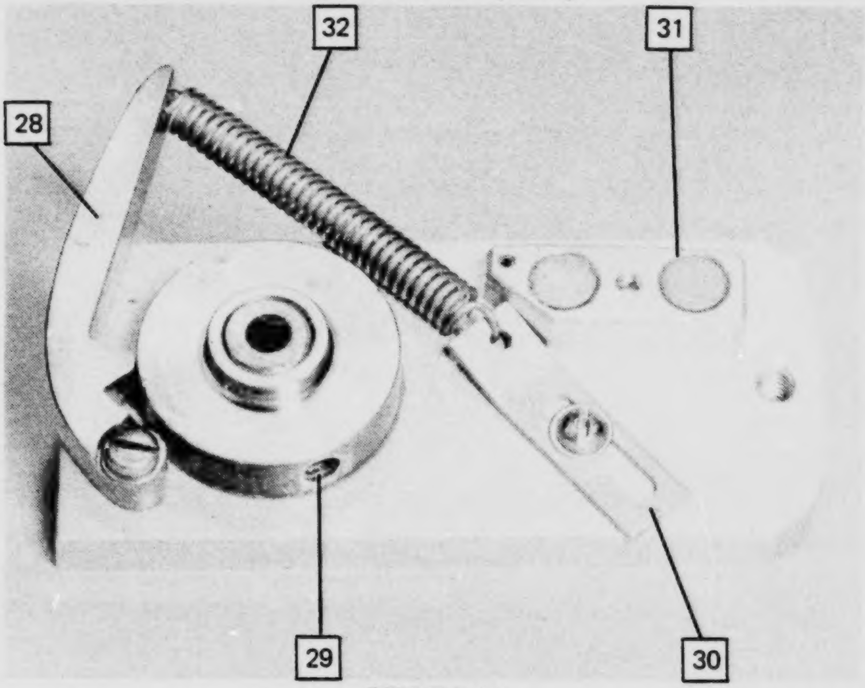

32
31
28
29
30

PHOTO #6
CLUTCH ARM

4.0. TROUBLESHOOTING

4.1. Sensor Unit

4.1.1. "What It Does."

The sensor unit has two functions: to initiate the movement of the collector lid by activating the motor box unit (when the start and stop of precipitation is detected), and to regulate two heating modes, the ambient mode to melt snow and the wet collect mode to dry water from the wetted sensor.

Activating Motor Box Unit

When water fills the space between the sensor grid (5) and plate (6) (rain begins), the sensor unit activates the motor box unit to move the collector lid over the dry-side bucket. This leaves the wet-side bucket exposed to capture precipitation. When water no longer fills this space (the rain slows or stops), the motor box is once again activated and the collector lid returns to the wet-side bucket. This leaves the dry-side bucket exposed. In serving this function the sensor unit is acting as a simple on/off switch.

Regulating Sensor Heating Modes

A heater fixed to the sensor plate is activated when the ambient air temperature falls below 4°C (40°F) or when the collector lid is covering the dry-side bucket.

The ambient heater mode is controlled by a temperature sensitive electrical component called a thermistor, mounted to the sensor plate. This component turns on the heater at a low power setting when the sensor plate drops below 4°C (40°F) and turns it off again when the plate warms above that temperature. In this fashion the heater melts snow and ice so that the resulting liquid can bridge the sensor grid and plate, allowing the collector to open.

The **wet collect mode** of the sensor heater is activated when the collector lid is covering the dry side bucket due to a wetted sensor. In this position, the event recorder/wet mode heater switch on the left side of the drive motor shaft (27) is tripped by the clutch unit switching magnets (31). This turns on both the wet collect mode of the sensor heater and energizes the event recorder terminal (19) with a 15 ± 3 volt DC current. In this mode the thermistor attached to the sensor plate budgets the current flow to the heater so that the plate temperature is regulated to a 60°C maximum. Five to ten minutes pass after the heater has been activated before it reaches full heat.

4.1.2. "What Goes Wrong."

When the sensor unit is faulty, some of the following symptoms may be observed:

Symptom	See Flow Chart
Collector lid stays over the dry-side bucket long after precipitation stops, sensor dries slowly (more than 30 minutes for rain), motor not running. (If motor is running, see **Clutch Unit - "What Goes Wrong"**.)	#1, page C-19
Collector lid oscillates non-stop between buckets, sensor wet or dry.	#5, page C-23
Collector lid stays over wet-side bucket, sensor wet, motor not running. (If motor is running, see **Clutch Units - "What Goes Wrong"**.)	#6, page C-24
Collector lid stays over dry side bucket, sensor dry, motor not running. (Again, if motor is running, see **Clutch Units - "What Goes Wrong"**).	#4, page C-22
Sensor plate (6) snow covered or iced up.	#3, page C-21

4.2. Motor Box Unit

4.2.1. "What It does."

The motor box unit (9) houses a drive motor, power and control circuitry, and fuses (22, 23, and 24). One visible side of the unit is occupied by connectors, such as the sensor unit socket (20), event recorder terminal (19), etc., (see Photo #4). The other side (see Photo #5) is occupied by the drive motor shaft (27) and three switching magnets (25 and 26).

The motor box main function is to power the lid mechanism between the wet and dry-side buckets, interacting with the clutch and sensor unit to control the lid position.

Power Function

In order to move the lid mechanism from bucket to bucket, the collector uses a small DC electric motor and gear cluster. These exit the motor box at the drive motor shaft (27). This shaft is a steel, half-round component to which the clutch arm unit (10) is fastened. Force is transferred through the clutch arm and a long push rod (14) to the lid drive arms (16). These lid drive arms, in turn, exit out the top of the collector mainframe and attach to the lid or roof of the collector.

Motor Box/ Clutch Interaction

As previously mentioned, the sensor unit acts as the "on" switch to tell the motor box to move the lid to the dry bucket (or conversely as an "off" switch which causes the collector to move the lid to the wet bucket). The motor box components responsible for this interaction are the clutch arm switching magnets (31) and the motor box stop switches (25).

When the motor box receives a "wet" signal the dry collect stop switch, the one to the right of the motor shaft in Photo#5, releases. The clutch arm then moves counterclockwise stopping at the wet collect stop switch, which operates in tandem with the event recorder/wet mode heater switch (see 25 and 26). The clutch arm should stay in this position until the sensor signals "dry." This allows the wet collect stop switch to "release" and the mechanism to power to the dry collect stop switch, causing the wet collect bucket to be covered.

4.2.2. "What Goes Wrong."

When the motor box unit is faulty, some of the following symptoms may be observed:

Symptom	See Flow Chart
Collector lid stays over the dry-side bucket long after precipitation stops, sensor dries slowly (more than 30 minutes for rain), motor not running. (If motor running, see **Clutch Unit - "What Goes Wrong."**)	#1, page C-19
Collector lid stays over wet-side bucket, sensor wet, motor not running. (If running, see **Clutch Unit - "What Goes Wrong."**)	#4, page C-24
Collector lid stays over dry-side bucket, sensor dry, motor not running. (If running, see **Clutch Unit - "What Goes Wrong."**)	#4, page C-22
Collector lid oscillates non-stop between buckets, sensor wet or dry.	#5, page C-23

4.3. Clutch Unit

4.3.1. "What It Does"

The clutch unit (10) has two main functions: (1) to act as a mechanical break or "fuse" in the drive system of the collector, and (2) to signal to the motor box the position of the lid of the collector, (i.e., the wet or dry mode).

Fusing the Drive System

The clutch serves to protect the rest of the drive train from any damage due to a stoppage. Such cases are generally caused by freeze downs, gross collector damage from blow-over or tree limbs, or from snow mounding high on the flat lids or on unheated snow roofs. In these cases the clutch works as follows (see Photo#5): from its normal position with the clutch tooth (28) in the indent of the thrust collar (29), the tooth "pops out" of the indent. After the full rotation of the thrust collar the tension spring will again pull the tooth into the indent, beginning the cycle anew. Since the thrust collar should be secured to the motor shaft by the set screw (29) the thrust collar *must* turn with the motor shaft. For efficient operation, the clutch tooth tension spring (32) is stretched so as to hold the clutch tooth into the thrust collar indent. In this way the force produced by the drive motor shaft is then transferred through the clutch to the rest of the collector lid drive mechanism. In addition the clutch locks this mechanism, keeping the lid tightly secured over the appropriate sampling bucket.

Signaling the Motor Box

As mentioned in the motor box unit description, the clutch interacts with the motor box stop switches (25) to control the position of the lid mechanism. In order to properly signal the stop switches, switching magnets (31) are built into the clutch arm; their position reflects the relative position of the lid mechanism. As the clutch arm and hence the lid mechanism near their stop positions, the appropriate switch releases or activates to fix the lid over either the wet or dry bucket (see Photos#5 and #6).

4.3.2. "What Goes Wrong"

When the clutch unit is faulty or out of adjustment, some of the following symptoms may be observed:

Symptom	**Cause**
Motor running, lid mechanism not moving. (Collector on wet side, dry side or in between.)	In this case the clutch mechanism is probably worn or out of adjustment. It should be serviced using the following steps: 1. Remove the clutch arm machine bolt (11), thus separating the clutch unit from the rest of the collector lid mechanism. 2. Loosen the thrust collar set screw (29) and gently pry the clutch unit off the drive motor shaft (27). NOTE: To expose the set screw, simply start the motor running, stop the clutch arm with your hand, and unplug the collector when the set screw becomes visible.

Symptom

NOTE: The clutch spring should not be stretched so far as to "freeze" the clutch. The drive motor has a maximum torque rating and can be damaged if the clutch will not "pop out." After resetting the tension spring, be certain the clutch can still be popped out by the drive motor.

Cause

3. Examine the clutch unit: if the thrust collar indent or the clutch tooth (28) appear severely rounded then the clutch probably merits replacement. (Call the CAL.) If they do not, then the force with which the tooth is held into the indent should be increased.

4. ADJUSTING THE CLUTCH TOOTH TENSION SPRING. The tooth/indent pressure is adjusted via the position of the clutch tooth tension plate (30). The further away from the thrust collar the plate is pushed, the more tension is produced.

a) Mark the tension plate's original position with a pencil;

b) Loosen the tension plate screw;

c) Move the plate out 1/4";

d) Test the clutch (see NOTE aside);

e) Slide clutch unit back into the drive shaft and tighten the set screw;

f) Plug in the collector and hold the clutch unit to make certain it will function as described;

g) Re-attach the machine bolt and drive arm of the lid mechanism.

Some trial and error may be necessary to reach an appropriate clutch spring tension.

Symptom	Cause
Collector will not shut off, continually cycling between buckets.	In this case the motor box has malfunctioned (reference Flow Chart #5) or the clutch unit position is incorrect. In order to properly signal the motor box unit, the clutch must be within 1/4-inch. This is necessary so that the switching magnets are close enough to trigger the motor box stop switches (25) and the event recorder/wet mode heater switch (26). To be certain the clutch is on all the way, loosen the set screw (29) and gently tap the clutch with a small hammer or screwdriver handle, then retighten the set screw.

The next section is a series of flow charts which should be useful in diagnosing the problems with a malfunctioning collector.

4.4. Flow Charts

Below are listed the most common failure symptoms experienced with the Aerochem Metrics Wet/Dry Precipitation Collector, at least those that most often come to our attention here at the CAL. Hopefully this list can refer you to an appropriate flow chart so that you can begin the trouble shooting steps necessary to get your collector back into operation.

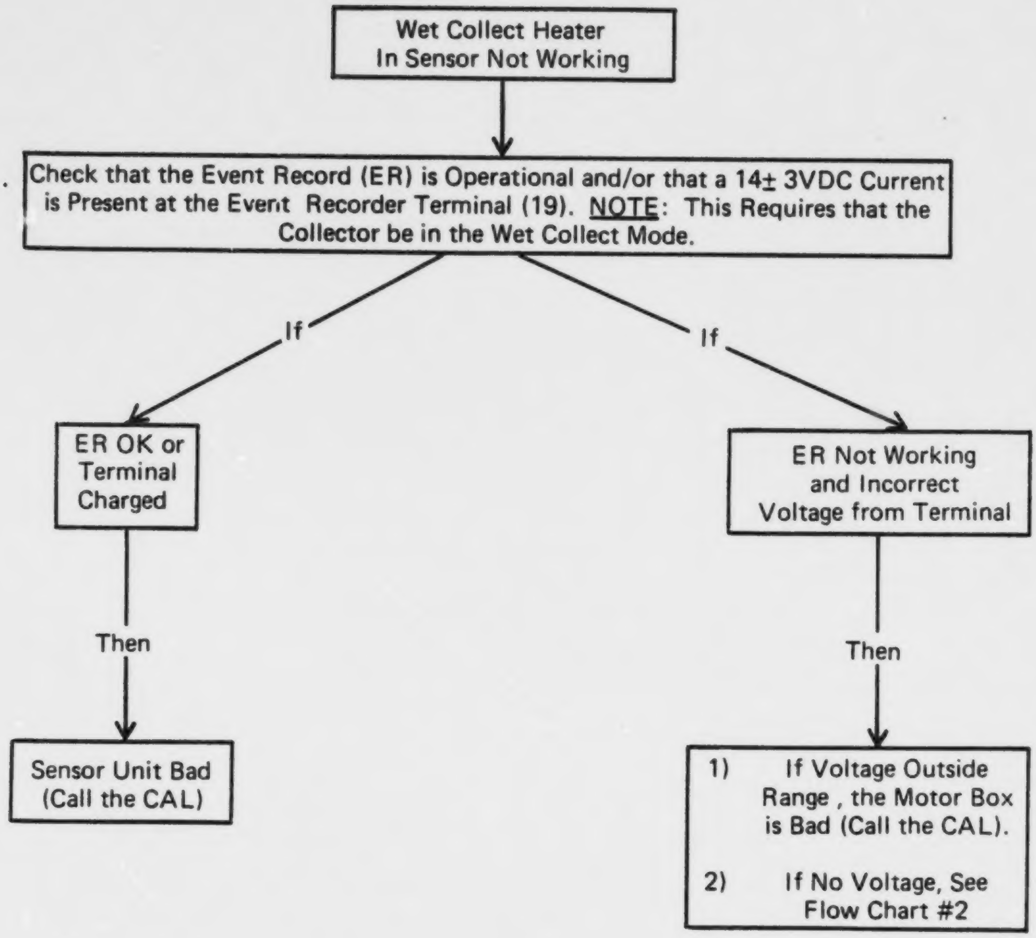
Symptom	See Flow Chart
Collector stays open long after precipitation event ends	1
Event recorder not working	1 and 2
Sensor ices up during cold weather	3
Collector stuck over dry-side bucket	4
Collector cycling continuously	5
Collector stays on wet-side bucket although sensor grid and plate are shorted	6

**NOTE:

ALL OF THE FOLLOWING FLOW CHARTS ASSUME THAT THERE IS ADEQUATE POWER TO THE UNIT AND THAT THE FUSES ARE INTACT.

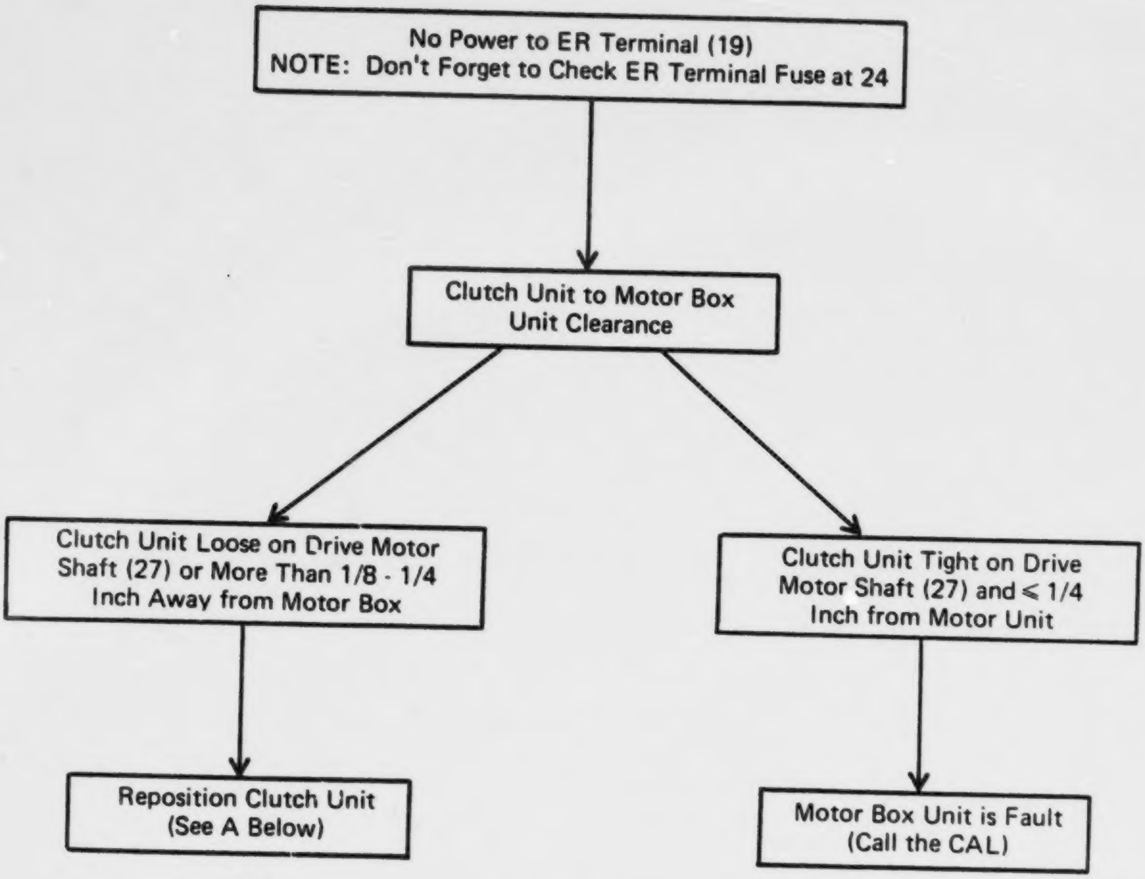
FLOW CHART #1

COLLECTOR STAYS OPEN LONG AFTER PRECIPITATION EVENT STOPS


Wet Collect Heater In Sensor Not Working
Check that the Event Record (ER) is Operational and/or that a 14± 3VDC Current is Present at the Event Recorder Terminal (19). NOTE: This Requires that the Collector be in the Wet Collect Mode.
If
If
ER OK or Terminal Charged
ER Not Working and Incorrect Voltage from Terminal
Then
Then
Sensor Unit Bad (Call the CAL)
1) If Voltage Outside Range , the Motor Box is Bad (Call the CAL).
2) If No Voltage, See Flow Chart #2

FLOW CHART #2

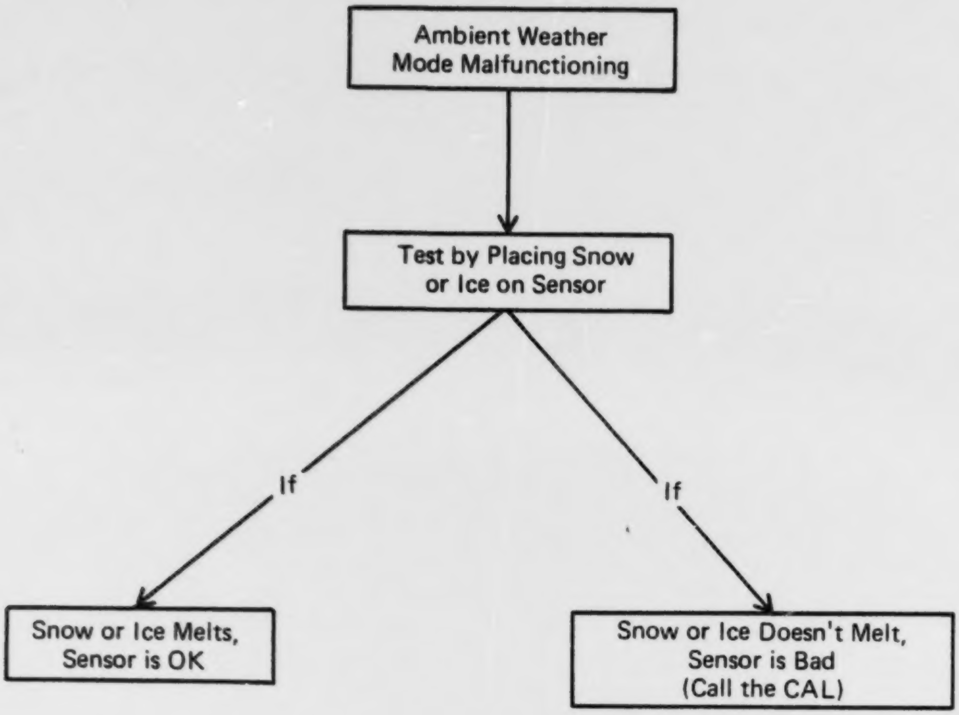
EVENT RECORDER NOT WORKING


No Power to ER Terminal (19)
NOTE: Don't Forget to Check ER Terminal Fuse at 24
Clutch Unit to Motor Box Unit Clearance
Clutch Unit Loose on Drive Motor Shaft (27) or More Than 1/8 - 1/4 Inch Away from Motor Box
Clutch Unit Tight on Drive Motor Shaft (27) and ≤ 1/4 Inch from Motor Unit
Reposition Clutch Unit (See A Below)
Motor Box Unit is Fault (Call the CAL)

A problem exists if the clutch unit is too far from the motor box unit. The magnets in the clutch can only trip the switches in the motor box if they are within ¼ inch. See Section C 4.3 for more information on clutch position.

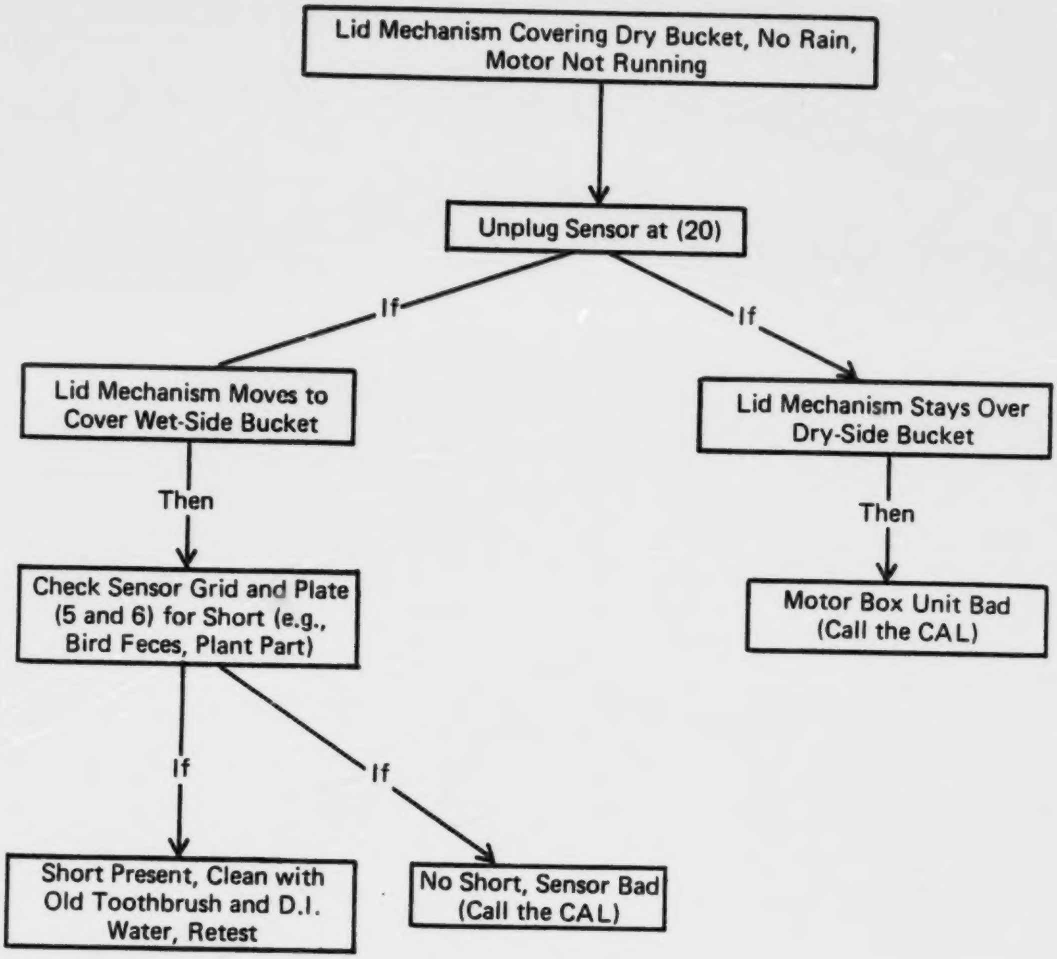
FLOW CHART #3

SENSOR ICES UP IN COLD WEATHER AND SNOW


Ambient Weather Mode Malfunctioning
Test by Placing Snow or Ice on Sensor
If
If
Snow or Ice Melts, Sensor is OK
Snow or Ice Doesn't Melt, Sensor is Bad (Call the CAL)

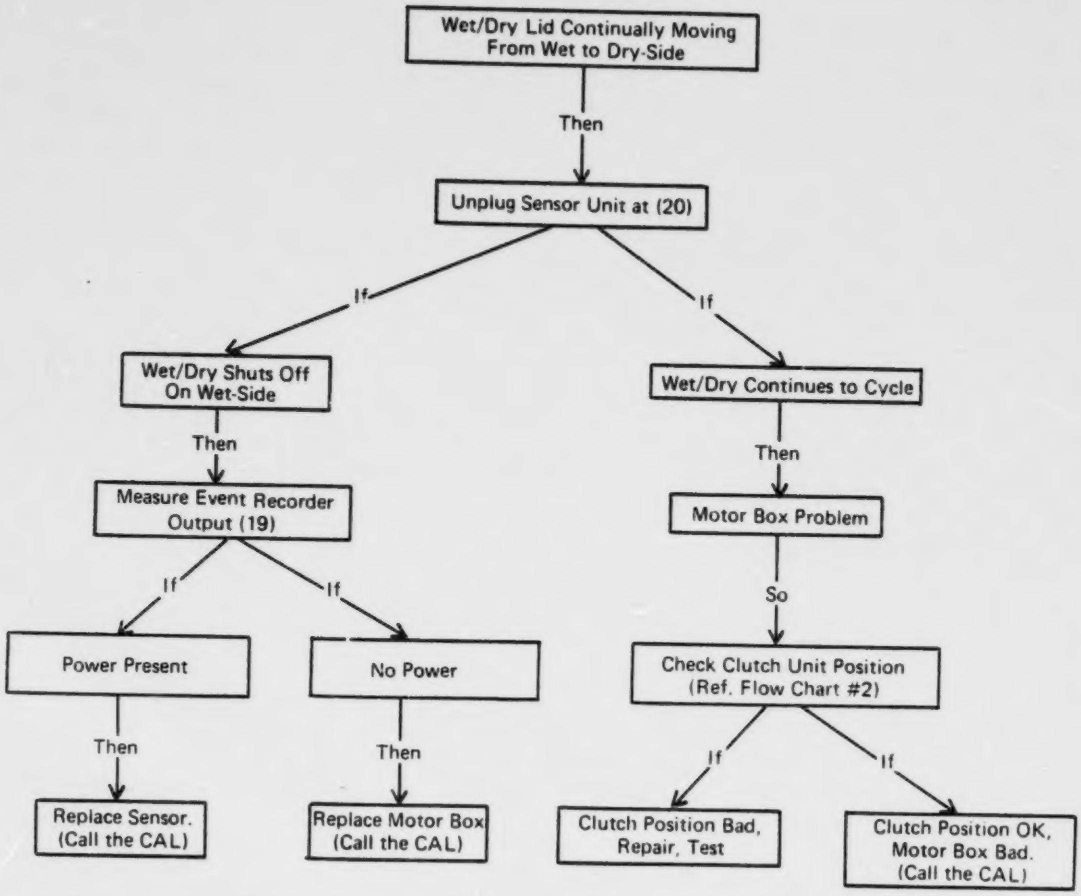
FLOW CHART #4

COLLECTOR STUCK OVER DRY-SIDE BUCKET


Lid Mechanism Covering Dry Bucket, No Rain, Motor Not Running
Unplug Sensor at (20)
If
If
Lid Mechanism Moves to Cover Wet-Side Bucket
Lid Mechanism Stays Over Dry-Side Bucket
Then
Then
Check Sensor Grid and Plate (5 and 6) for Short (e.g., Bird Feces, Plant Part)
Motor Box Unit Bad (Call the CAL)
If
If
Short Present, Clean with Old Toothbrush and D.I. Water, Retest
No Short, Sensor Bad (Call the CAL)

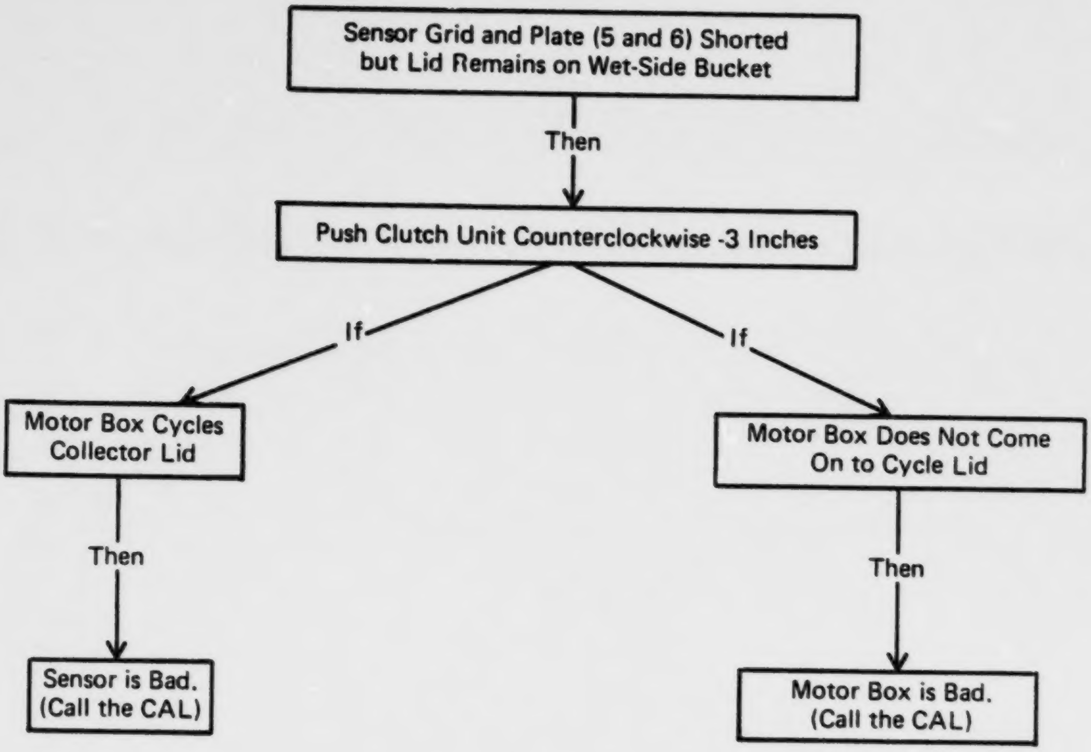
FLOW CHART #5

COLLECTOR CYCLING CONTINUALLY


Wet/Dry Lid Continually Moving From Wet to Dry-Side
Then
Unplug Sensor Unit at (20)
If
If
Wet/Dry Shuts Off On Wet-Side
Wet/Dry Continues to Cycle
Then
Then
Measure Event Recorder Output (19)
Motor Box Problem
If
If
So
Power Present
No Power
Check Clutch Unit Position (Ref. Flow Chart #2)
Then
Then
If
If
Replace Sensor. (Call the CAL)
Replace Motor Box (Call the CAL)
Clutch Position Bad, Repair, Test
Clutch Position OK, Motor Box Bad. (Call the CAL)

FLOW CHART #6

COLLECTOR NOT OPENING TO EXPOSE WET-SIDE IN HEAVY RAINFALL


Sensor Grid and Plate (5 and 6) Shorted but Lid Remains on Wet-Side Bucket
Then
Push Clutch Unit Counterclockwise -3 Inches
If
If
Motor Box Cycles Collector Lid
Motor Box Does Not Come On to Cycle Lid
Then
Then
Sensor is Bad. (Call the CAL)
Motor Box is Bad. (Call the CAL)

5.0. COMPONENT REPLACEMENT AND ROUTINE SERVICING

5.1. Component Replacement

5.1.1. Motor Box Unit

This component can be removed by separating the sensor plug from the sensor socket (20), removing the clutch arm machine bolt (11), and then removing the four motor box attachments (7) from the collector main frame (2). Threaded inserts are used in the motor box so there are no nuts to replace.

WARNING: The motor box will literally fall out when the last of the four screws are removed. Make plans to support it in some fashion.

Last, with the box on the ground and in easy access, remove the event recorder leads from their terminal (19).

5.1.2. Sensor Unit

This component is easily removed by separating the sensor socket (20) from the sensor plug in and removing the four sensor attachements (3). Again, the main frame is equipped with threaded inserts so there are no nuts to contend with.

5.1.3. Clutch Unit

The clutch can be removed from the motor drive shaft by choosing an appropriately sized Allen wrench and loosening the set screw at (29). Then simply pry the clutch assembly off using a sturdy screwdriver. Please reference page C-16 of this manual for additional remarks concerning replacement and maintenance.

Remember to return all used components to the manufacturer promptly.

5.2. Routine Servicing

In general, the Aerochem Metrics wet/dry collector is maintenance free. The one routine service chore which all sites should perform is the testing of the sensor "switching" and heating functions. It is recommended that these tests be incorporated into weekly wet-side bucket changes using the steps listed below.

a. First, feel the sensor grid. Assuming it has not been raining, it should be cool.

b. **Short the sensor grid and plate** with water (water is better than metal for this test, due to its lower conductivity).

c. **Allow the lid mechanism to move over and cover the dry-side bucket.** This step (1) checks the switching function of the sensor, (2) checks the lid driving mechanism of the collector, and (3) keeps the lid mechanism out of the way while you make your bucket change.

d. **Change buckets**, (See Section 3.2.2.)

e. **After the collector has been open for at least 5 minutes, feel the sensor grid.** In all but very cold temperatures the heater should be easy to feel.

f. Blow remaining water off the sensor, allowing the lid mechanism to return to the wet-side bucket and the motor box to shut off.

5.3. Other Routine Servicing Suggestions

a. Periodically clean the sensor grid to remove any accumulation of minerals or contamination that could close the circuit and thus present a false "wet" signal. To clean the space between the grid and the plate, cut a strip of cardboard from a time card or a Manila folder to a width of about 1.8 inches (4.5 cm); this can be passed between the Teflon washers which fix the separation of the grid and plate, or, simply use an old toothbrush and deionized water or alcohol to remove accumulated material.

b. As needed, clean the lid, roof and arm mechanisms to remove any residues (e.g., bird feces, dust, other organic material).

Appendix D
Belfort Recording Rain Gage
Model B5-780
Maintenance Manual

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1.0. INTRODUCTION

The Belfort recording rain gage is a device which converts the weight of precipitation (collected by an internal catch bucket) into an up-and-down motion of a recording pen on a paper chart. This instrument is widely used by national and state-level monitoring networks because of its ability to provide good resolution of precipitation timing and amount during a recording period, and its ability to provide hard copy of that data.

This guide is intended to address troubleshooting and checking of the instrument as pertinent to NADP/NTN monitoring program. It does not provide detailed information on calibration or other related mechanical systems within the rain gage.

For purposes of brevity the Belfort 5-780 will hence forth be referenced by the words GAGE or RAIN GAGE and the Aerochem Metrics Wet/Dry Precipitation Collector will be referenced as ACM.

IF YOU EXPERIENCE A RAIN GAGE MALFUNCTION PLEASE INFORM THE CAL:

(1) call the CAL at 217/333-0249

(2) briefly describe the malfunction and indicate its occurrence on the Field Observer Report Form for that sample. Continue to do this for each sample affected until the malfunction is eliminated. If you use auxiliary precipitation information please remark on the field form the type of rain gage substituted and its approximate distance from the wet-dry precipitation collector.

Example: Rain gage clock stopped on Thursday. Took precipitation from 8" stick gage, measured daily at 0800, 25' away.

2.0. PARTS REFERENCE LIST

This list identifies parts by name and assigns part numbers that are used in conjunction with the "Pictorial Guide to Parts" section which follows. Also, all part numbers are cross-referenced to a corresponding photo number.

Some part numbers are referenced in the "Trouble Shooting" section of this text. Individual part numbers are signified by parenthesis throughout the text (e.g. (1)=Catch Bucket).

Part name	Part No.	Photo No.
Catch Bucket	1	1
Zero Adjustment Screw(s) and Setting Bar	2	1 and 2
Limit Screw(s)	3	1 and 2
Fine Linkage	4	2
Precipitation Pen Arm	5	1
Mechanism Base	6	1 and 2
Pen Tip	7	1 and 2
Pen Shifter	8	1
Chart Drum with Clip	9	1
Bucket Platform	10	1 and 2
Top Lever	11	1 and 2
Dashpot	12	2
Clock (Beneath Chart Drum)	13	1
Precipitation Pen Arm Stud	14	1
Event Recorder	15	1 and 2
Bucket Support Shaft	16	1 and 2
Top Cap	17	3
Funnel	18	3
Event Recorder Solenoid	19	4
Event Recorder Pen and Arm	20	4
Event Recorder Pivot Point	21	4
Event Recorder L-Bracket	22	4
Clock Body	23	5
Output Shaft	24	5
Clock Gear	25	5

Components on Facing Page

Part Number	Name
1	Catch Bucket
2	Zero Adjustment Screw(s) and Setting Bar
3	Limit Screw(s)
5	Precipitation Pen Arm
6	Mechanism Base
7	Pen Tip
8	Pen Shifter
9	Chart Drum With Clip
10	Bucket Platform
11	Top Lever
13	Clock
14	Pen Arm Stud
15	Event Recorder
16	Bucket Support Shaft

3.0. PICTORIAL GUIDE TO PARTS

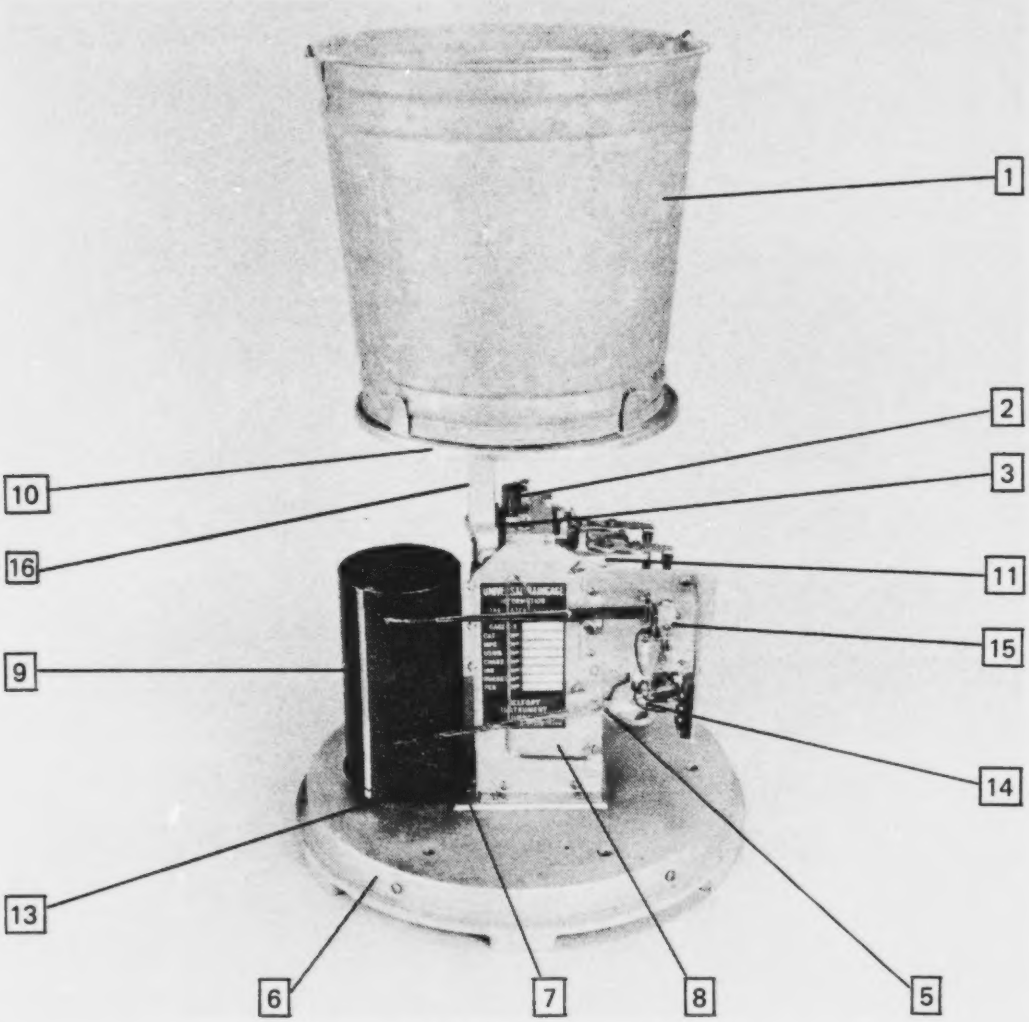

1
2
3
10
16
11
15
9
14
13
6
7
8
5

Photo 1. Rain Gage General View

Components on Facing Page

Part Number	Name
2	Zero adjustment screws and setting bar
3	Limit screws
4	Fine Linkage
6	Mechanism Base
7	Pen Tip
10	Bucket Platform
11	Top Lever
12	Dashpot
15	Event Recorder
16	Bucket Support Shaft

Reproduced from
best available copy.

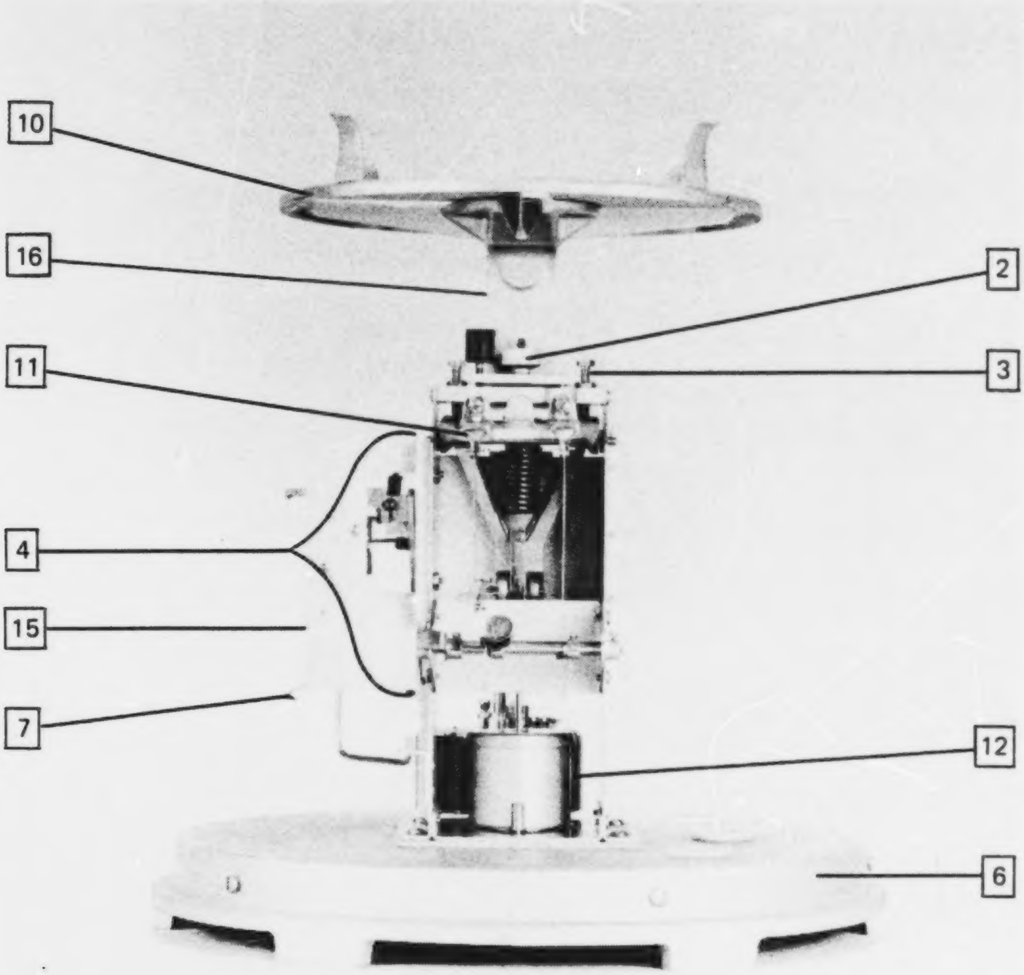

10
16
2
11
3
4
15
7
12
6

Photo 2. Rain Gage Detailed View

Components on Facing Page

Part Number	Name
17	Top Cap
18	Funnel
19	Event Recorder Solenoid
20	Event Recorder Pen and Arm
21	Event Recorder Pivot Point
22	Event Recorder L-Bracket

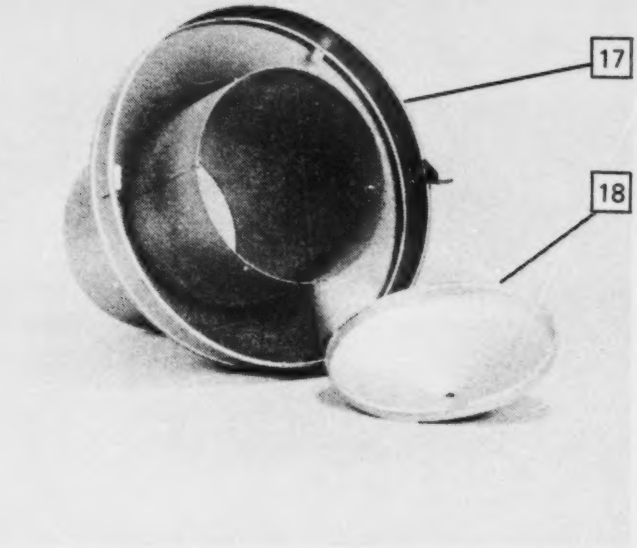


Photo 3. Top Cap and Funnel Assembly

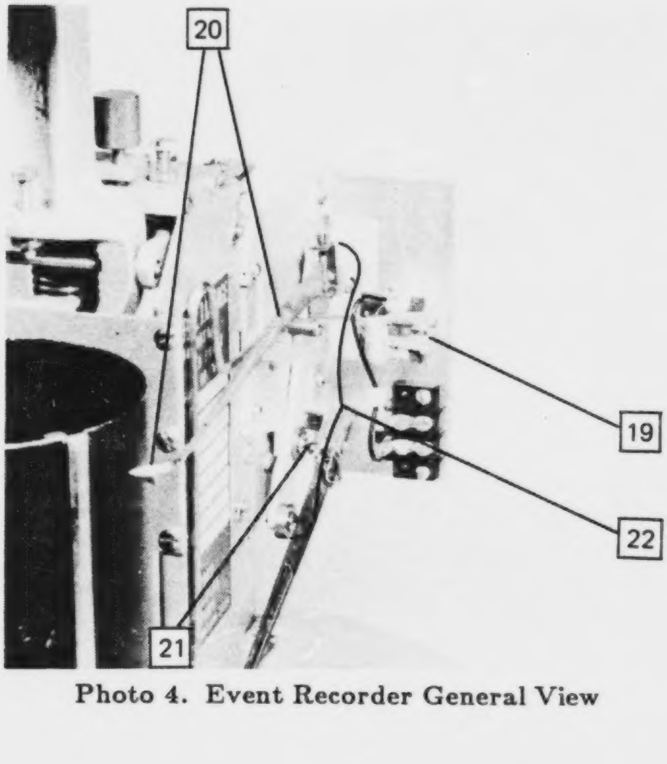


Photo 4. Event Recorder General View

Components on Facing Page

Part Number	Name
23	Clock Body
24	Output Shaft
25	Clock Gear

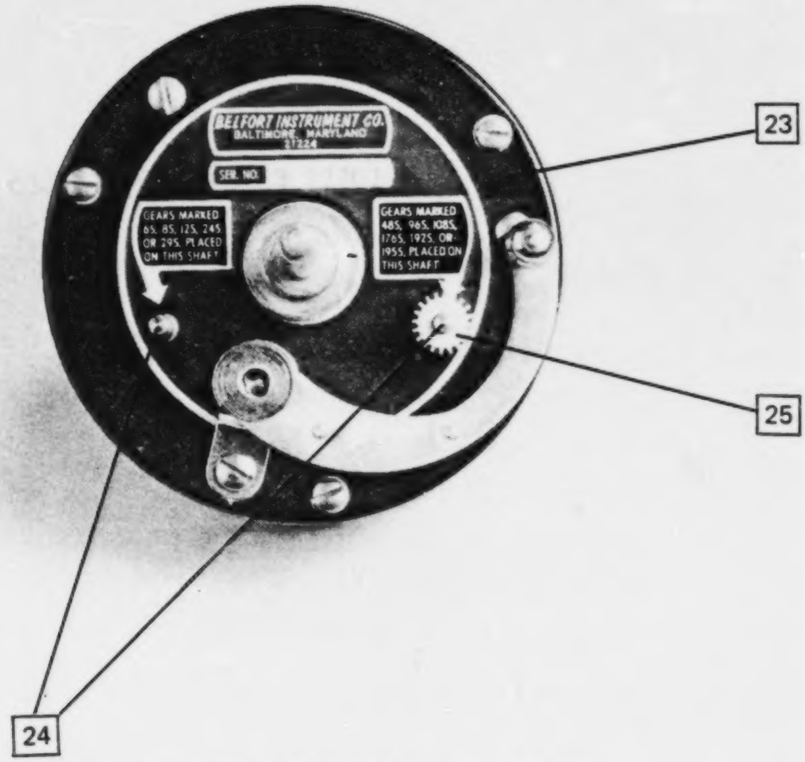

BELFORT INSTRUMENT CO.
BALTIMORE, MARYLAND
21224
SER. NO.
GEARS MARKED 6S, 8S, 12S, 24S, OR 29S, PLACED ON THIS SHAFT
GEARS MARKED 48S, 96S, 108S, 176S, 192S, OR 195S, PLACED ON THIS SHAFT
23
25
24

Photo 5. Clock Top View (with gear in place)

4.0. TROUBLESHOOTING

For the purposes of this manual the weighing and writing mechanisms of the rain gage and the event recorder mechanism (which is shared between the rain gage and the ACM) will be presented as two distinct subsections within Troubleshooting. Most of the parts and systems discussed are visible from the door of the rain gage.

4.1. Event Recorder Unit - "What It Does."

The event recorder takes a 12-volt DC power signal produced by the motor box of the ACM and converts it into an up-and-down record on the rain gage chart. The purpose of the event recorder is to allow site and laboratory personnel to evaluate the open/close cycles of the precipitation collector in relation to the incidence of precipitation.

As DC power energizes the event recorder solenoid (19) the solenoid activates the event recorder L-bracket (22) and thus the event recorder pen and arm (20). This means that the wet-side bucket of the precipitation collector is exposed. After an event subsides and the ACM closes the solenoid is de-energized and the mechanism drops down in response to gravity.

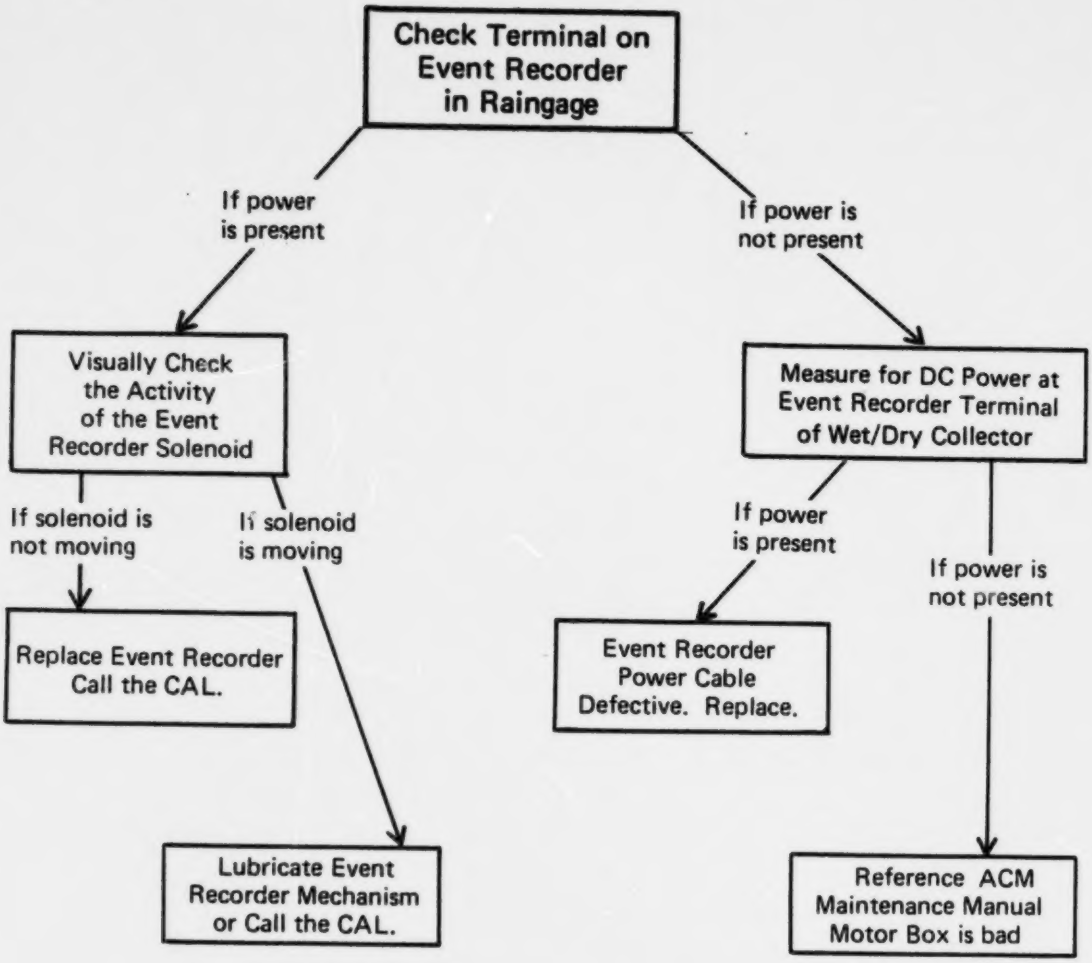
4.2. Event Recorder Unit - "What Goes Wrong."

Malfunctions of the event recorder are often traced to a source external to the rain gage itself. Typically these are the ACM or the cable connecting it to the gage. CAUTION: Thoroughly check those external systems prior to spending lots of time on the event recorder (reference Appendix C, Aerochem Metrics Maintenance Manual).

When the event recorder itself does break, the malfunctions typically fall into two categories: 1) Failure to rise upon power supply; and 2) Failure to drop upon power reduction (see Flow Chart #1).

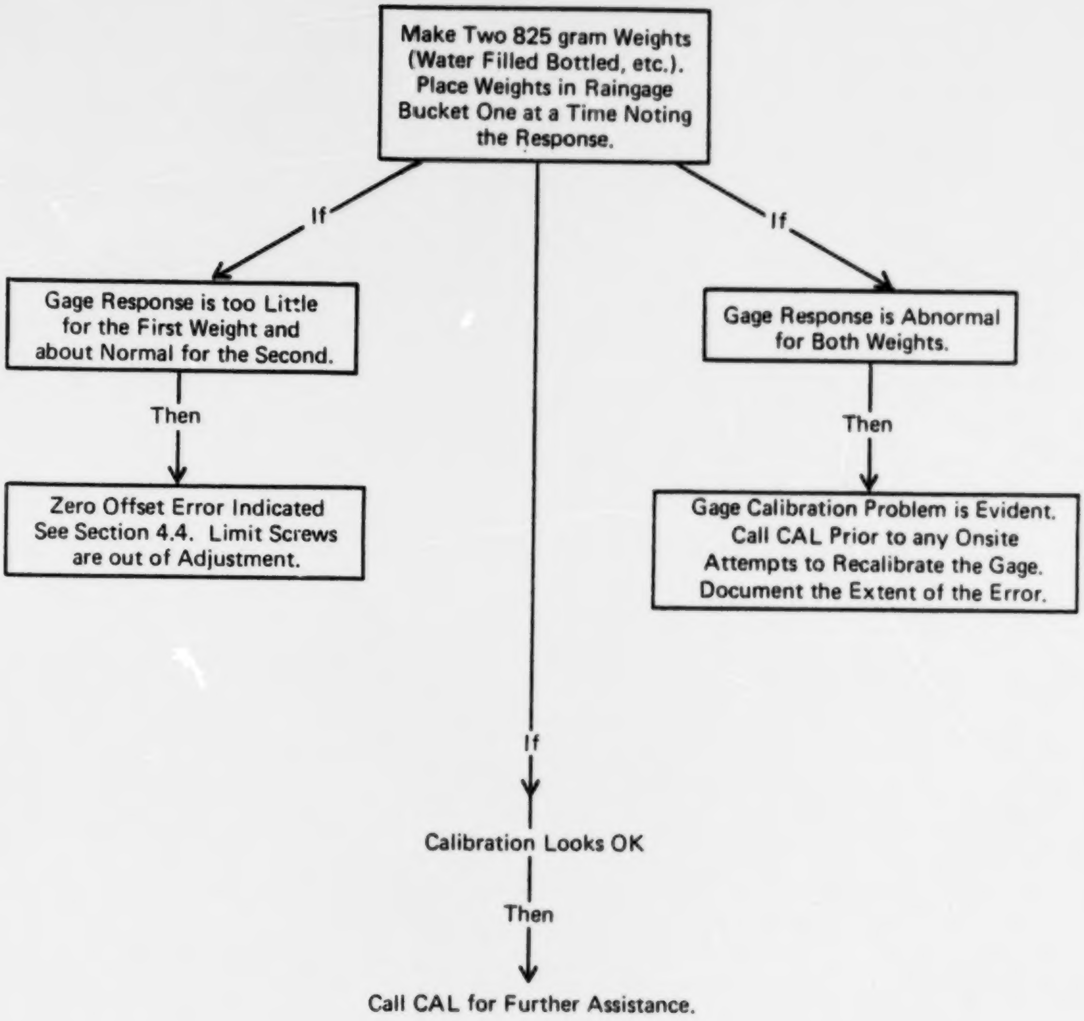
FLOW CHART #1

EVENT RECORDER TRACE DOES NOT COINCIDE WITH THE OCCURRENCE OF PRECIPITATION


Check Terminal on Event Recorder in Raingage
If power is present
If power is not present
Visually Check the Activity of the Event Recorder Solenoid
Measure for DC Power at Event Recorder Terminal of Wet/Dry Collector
If solenoid is not moving
If solenoid is moving
If power is present
If power is not present
Replace Event Recorder Call the CAL.
Event Recorder Power Cable Defective. Replace.
Lubricate Event Recorder Mechanism or Call the CAL.
Reference ACM Maintenance Manual Motor Box is bad

FLOW CHART #2

RAINGAGE WEIGHING MECHANISM NOT CORRECTLY RESPONDING TO THE ADDITION OF PRECIPITATION TO THE CATCH BUCKET



Make Two 825 gram Weights (Water Filled Bottled, etc.). Place Weights in Raingage Bucket One at a Time Noting the Response.

Gage Response is too Little for the First Weight and about Normal for the Second.

Zero Offset Error Indicated See Section 4.4. Limit Screws are out of Adjustment.

Gage Response is Abnormal for Both Weights.

Gage Calibration Problem is Evident. Call CAL Prior to any Onsite Attempts to Recalibrate the Gage. Document the Extent of the Error.

Calibration Looks OK

Call CAL for Further Assistance.

4.2.1. Failure to Rise

Generally problems with the rising of the event recorder pen will not be due to the mechanical linkage but to a malfunction in the event recorder solenoid. To confirm this, examine the event recorder solenoid (19) for motion when it receives power. If a malfunction exists within the solenoid the event recorder must be replaced.

If power and motion have been confirmed at the event recorder terminal (15), the mechanical function of the event recorder pen and arm (20) and event recorder L-bracket (22) should be checked.

Simply move the pen arm up-and-down with your fingers, checking for freeness of the mechanism and the condition of the event recorder pivot point (21). If the mechanical linkage appears to be binding and thereby reducing the motion of the pen, lubricate the pivot point (21) in order to achieve the motion required. NOTE: Only Silicon or Teflon based aerosol lubricants should be used. By using the tube which comes with these types of aerosols you can irrigate (clean) and lubricate the pivot point at the same time.

4.2.2. Dropping of the Event Recorder Pen

As opposed to the powered function of its rising, the dropping of the event recorder depends entirely on the force of gravity. The weight of the pen and pen arm (20) and the L-bracket (22) on the pivot point cause the pen to move down.

If the dropping function is impeded, lubricate the pivot point (21) and attempt to work the mechanism free. If this does not solve the problem additional weight must to be added to the event recorder mechanism. Call the CAL for advice.

4.3. Rain Gage Weighing and Writing Mechanism - "What It Does"

Precipitation falling through the top section and into the catch bucket mounted on its support shaft causes the linkage at the rear of the instrument to rotate the shaft upon which the rain gage pen and arm are mounted. In this manner a series of levers and shafts, herein called the fine linkage, translates approximately 825 grams of precipitation into 1" of deflection at the pen. This deflection is marked on the chart by the pen tip which is filled with ink.

DO NOT ATTEMPT MODIFICATION OF THE CURRENT FINE LINKAGE SETTINGS.
INCORRECT SERVICING CAN CAUSE SEVERE DAMAGE TO THE MECHANISM.

4.4. Rain gage Weighing and Writing Mechanism - "What Goes Wrong"

The functions of the gage have been divided into two general categories:

(1) weighing functions - generally pertaining to the physical transfer of the precipitation weight to a pen motion; and

(2) writing functions - which consist of the pen accurately and dependably writing on the chart.

4.4.1. Weighing Functions

As previously mentioned the mechanism in the fine linkage of the rain gage is not to be modified. There are, however, several areas on the rain gage which may be checked in order to identify the area of malfunction. These areas include: the zero adjustment screws (2), limit screws (3), and the catch bucket (1).

When the weighing mechanism is faulty some of the following symptoms may be observed:

Symptoms	See Section
Rain gage pen marking erratically.	A and B (see Figures D-1 and D-2)
No response to weight addition into catch bucket or improper response.	B, C, or D (see Figures D-2 and D-4)
Poor collection efficiency (defined as wet/dry versus rain gage collection volume).	C or D (see Figure D-4 and D-5 and Flow Chart #2)

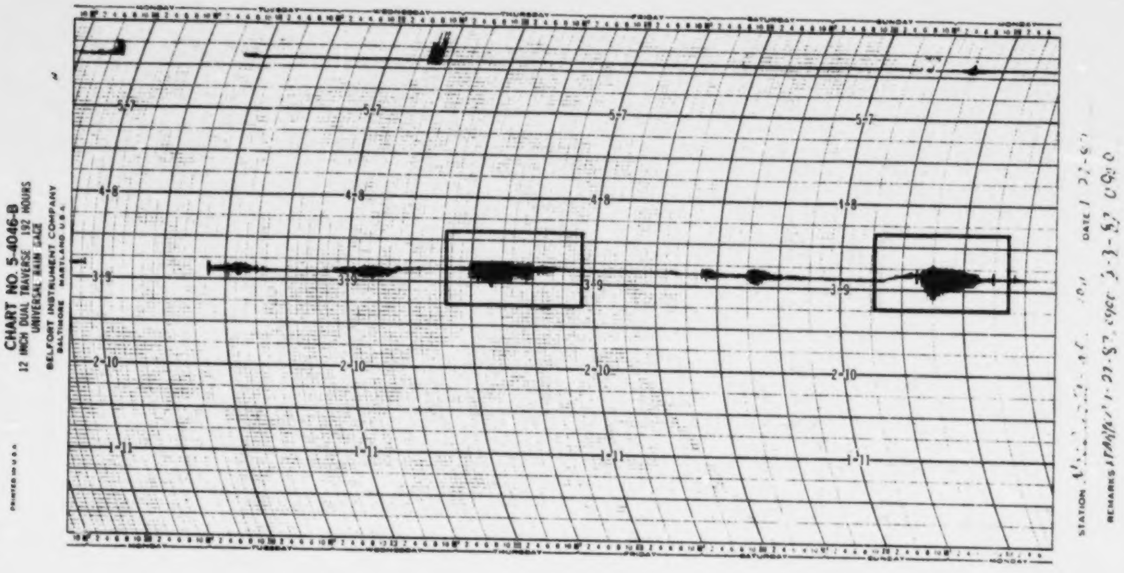
A. Wind Shake - (see Figure D-1).

This phenomenon is often caused by looseness of case or rain gage mounting bolts. Make certain all screws around the bottom of the "milk can" and mounting bolts are secure.

Check the level and quality of the dashpot (12) fluid. The dashpot serves as a "shock-absorber" in the rain gage linkage system. If the fluid level is insufficient it cannot dampen the motion of the bucket support shaft (16). In order to offer adequate performance the fluid in the dashpot must be above the level of the floating piston at its highest level. The dashpot fluid is available from the Belfort Instrument Company. For temporary emergency use automotive antifreeze can be substituted.

Figure D-1. Wind Shake

NOTE THE WIDE AND SPIKED NATURE OF THE TRACE IN THESE TWO INSTANCES
CHECK DASHPOT FLUID AND THE TIGHTNESS OF THE CASE
AND MOUNTING BOLTS.



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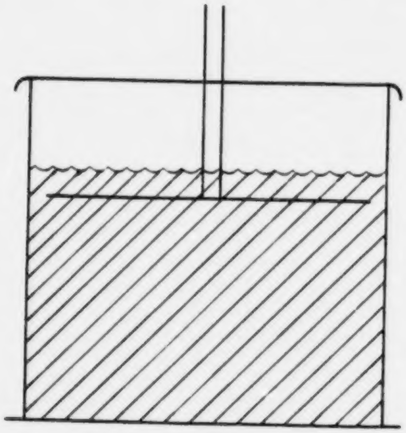
DASHPOT DETAIL SHOWING PISTON
AND APPROPRIATE LEVEL OF DAMPENING FLUID



B. Dashpot Freezing

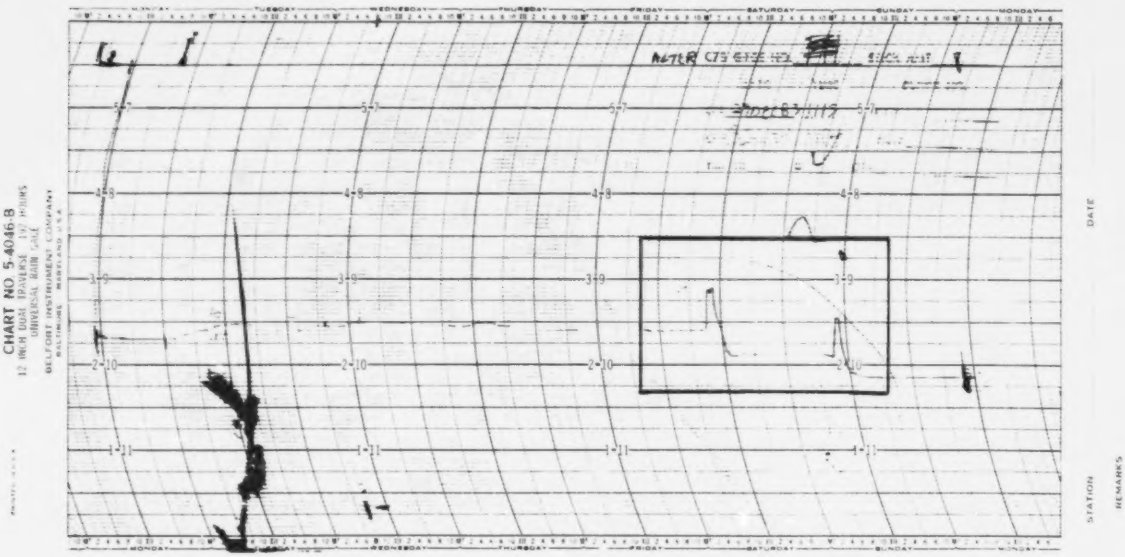
The wild up-and-down markings (as illustrated on Figure D-2) are indicative of frozen water within the dashpot mechanism. As temperatures drop any accumulated water (from blown-in snow or condensation) freezes and ice forms in the dashpot. The fine linkage is then subject to sudden and extreme motion. This situation should be resolved as soon as possible to prevent ruining the dashpot and invalidating precipitation data.

TO REPLACE DASHPOT FLUID

1. Open the sliding door of the rain gage.
2. Spin off the gage clock by turning it counterclockwise.
3. Remove the thumbscrew holding the dashpot (12) on the mechanism base (6).
4. Gently pull the dashpot body toward the door allowing the piston to gently pull up and out of the dashpot. See Dashpot detail in Figure D-1.
5. Empty the dashpot and wipe clean with a cloth, refill and replace.

Figure D-2. Rain Gage Dashpot Freezing

NOTE THE CRAZY WAVE PATTERN WITH SUDDEN PEAKS AND VALLEYS
AS ICE PUSHES PEN UP AND DOWN



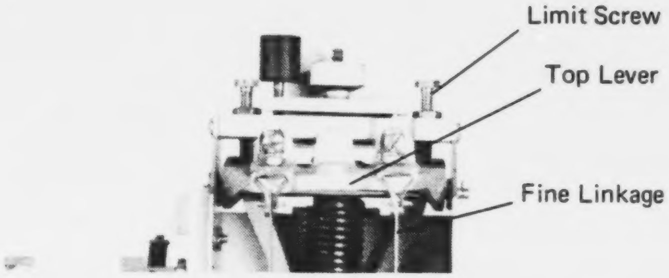
C. Incorrect or Lack of Response to Precipitation

The calibration mechanism of the rain gage is the most complex portion of the instrument. As previously mentioned, this manual will not discuss how to calibrate the gage. Three areas to evaluate are the catch bucket, limit screws and zero adjustment screws (see Flow Chart #2).

Catch Bucket. Difficulties in transferring weight to the rain gage mechanism through the bucket support shaft may be caused by the catch bucket rubbing against the top section (17) or funnel (18) of the rain gage. Check to be certain that the catch bucket bail (handle) and the catch bucket rim are not rubbing against the main housing of the rain gage. This condition will cause the main housing to absorb the weight of the precipitation, therefore not transferring it to the weighing mechanism. If this is the difficulty, a steel gray burnished area -where the contact has occurred- should be readily noticeable on the mechanism. Check to make certain the bucket platform (10) still supports the bucket squarely upon the support shaft, and remove the catch bucket bail if it is bent beyond repair.

Limit Screws. The limit screws (3) serve to lock the fine linkage (4) mechanism during shipment and to limit the travel of that linkage during extreme catch bucket loading (i.e., lots of rain). The limit screws can conflict with the top lever (11) when adjusted too far down, thereby preventing the mechanism from registering weight. The bottom of the limit screws should be separated from the top lever by a minimum of 1/16*inch* with the bucket empty. Confirming that "daylight" exists between the top lever and linkage should solve problems associated with the limit screws.

Figure D-3. Limit Screw Detail

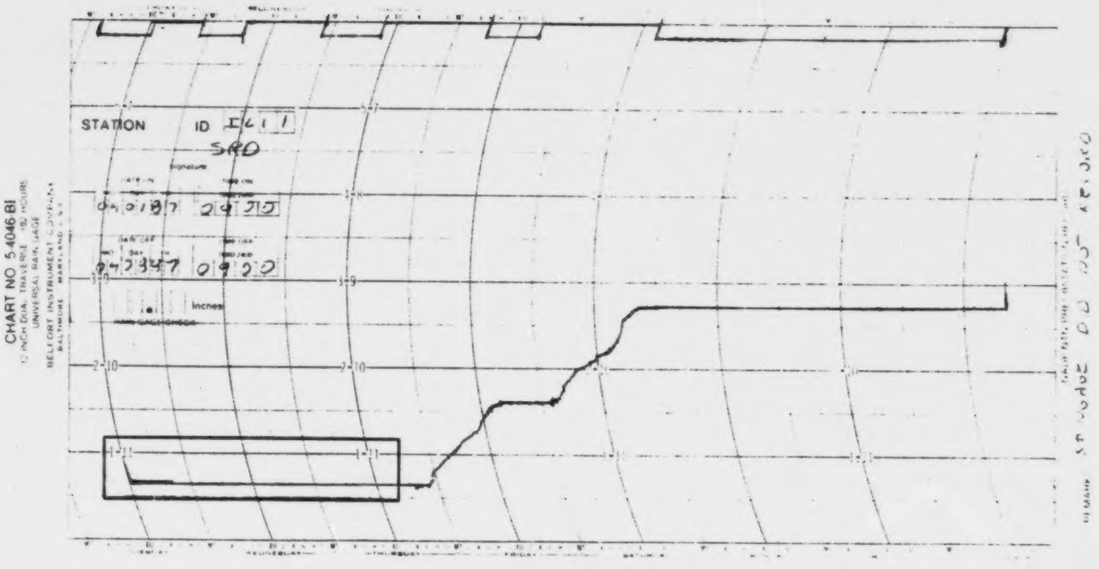


After adjustment firmly tighten the locking nut on the limit screw so that vibration of the case and contraction and expansion from heating and cooling does not cause the limit screws to move down onto the top lever again.

See Figure D-4. This figure illustrates the flat line nature of the rainfall amount pen for a rain gage afflicted by a limit screw defect. Note that the event recorder trace (which means precipitation was falling during a period) exists early in the week, yet no rainfall deflection can be seen.

Figure D-4. Limit Screw Adjustment Error

NOTE THE HIGH INITIAL BASELINE AND THE EVENT RECORDER TRACES EARLY IN THE PERIOD FOR WHICH NO RAINFALL IS SHOWN



Zero Adjustment Screws. These screws are often used to set the baseline of the gage pen. When turned, they cause the relationship between the top lever (11) and the limit screws (3) to be changed. CAUTION: When adjusting the zero adjustment screws make certain that; the limit screws maintain the correct distance from the top lever, and that the zero setting bar is approximately parallel to the gage housing. If either of the above factors are in error the gage may appear to undercatch precipitation.

Fine Linkage. At the bottom end of the fine linkage (4) there are two places where an oval shaped slot is cut into the link. These slots have a bolt riding through them. Inspect the area around and inside this slot to see if any worn areas, corroded patches or dirty spots exist. If so, the area will have to be cleaned and lubricated or replaced. Call the CAL for more details.

D. Poor Collection Efficiency

Collection efficiency (C.E.) is defined as the portion of precipitation collected in the ACM (PE) compared to the precipitation measured in the rain gage, or:

$$C.E. = PE/RG \times 100\%$$

where PE = the precipitation equivalent (sample weight in grams x .00058 inches/gram; and

RG = the weekly total amount of precipitation as measured on the recording rain gage chart

Typically C.E. values for rainfall range between 90% and 110%. Poor C.E.'s do not necessarily mean a malfunction in either mechanism. For example, the ACM is very susceptible to missing light rainfall and blowing snow. In addition, the rain gage is only able to resolve events to approximately 17 grams weight (.01 inch on the chart).

Assuming no problems related to Sections A, B, and C are found, it may be advisable to perform a calibration check upon the weighing bucket mechanism. This is especially true if the C.E. is consistently *greater than* 100% (ex., ACM - 1.25"; rain gage - 1.00"; in this case a 125% collection). Logic would dictate that the ACM cannot *make* precipitation. Therefore, the rain gage is *under measuring* the precipitation.

Calibration Check. *This procedure can be completed by non-technical personnel as long as accurate means of weighing are available.*

As mentioned before, the Belfort mechanism is calibrated to measure 1*inch* of water or precipitation equivalent (PE) for the addition of each 825 grams of weight. Any weight added to the rain gage catch bucket can be used to check the response of the mechanism.

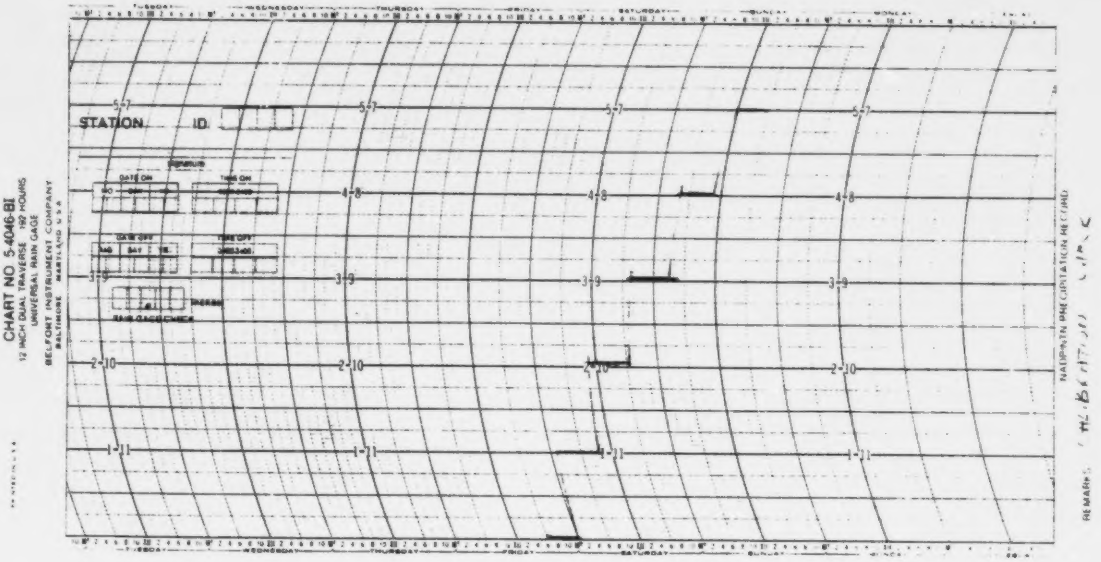
The Belfort Instrument Company offers a set of rain gage calibration weights. Contact the CAL for purchase information.

In lieu of a standard calibration weight set any pre-weighed mass can serve for calibration checking procedures. Remembering the 825 to 1 inch rule and using the following steps are all that is necessary.

1. Use your analytical balance to make up a set of weights (five-825 gram bottles for example).
2. After removing the rain gage chart from an ending sample period, install another rain gage chart labeled 'CALIBRATION CHECK' onto the drum.
3. Replace the drum upon the clock assembly and mark a base line with the pen assembly in order to define the beginning of your calibration check.
4. Add one rain gage weight to the catch bucket, then twist the chart drum to mark another base line value. The difference between the initial base line and the secondary base line should equal the deflection predicted by the weight (see Figure D-5).
5. Repeat step 4 above until the rain gage reaches approximately 5" of capacity. The effective range of measurement at most sites will be assured in this manner. If a suitable weight cannot be found, remember that one gram of water is equal to one milliliter of water. Therefore a volumetric calibration is possible. Call the CAL for details.

Figure D-5. Calibration Check

THE STAIR-STEP SHOWN REFLECTS THE ADDITION OF FIVE 1-INCH RAINGAGE WEIGHTS. NOTE THAT THERE IS A SMALL ERROR WITH THE ADDITION OF THE THIRD AND FOURTH WEIGHT. THE ERROR IS ONLY 0.02" HOWEVER. THIS GAGE IS IN ACCEPTABLE CALIBRATION.



If an error in excess of 0.10 inches is identified during the calibration check, contact the CAL. NADP/NTN lacks any 'quick response' mechanism whereby network representatives can come and assist you in the recalibration of the instrument. Local repair is suggested.

Regardless of the maintenance procedure or the amount of error encountered, please notify the CAL. Send along a copy of the Calibration Check rain gage chart. Data screening decisions may be based upon this information.

4.2.2. Writing functions

The writing functions of the recording rain gage break down into two general areas of concern: the rain gage pen (inking) capability and the rain gage clock assembly (which provides the time axis for writing). These two functions are separated in the section which follows.

Pen Function - The pens used on this rain gage fall into two general categories: (1) ink type pens (filled each week out of a reservoir bottle); and (2) felt tip pens. Because most sites use ink pens and because felt tip pens are easily replaced, only ink type pens will be covered in this section.

Typical problems associated with pen function include: 1) dirty or fouled tips due to long-term use and ink evaporation, and 2) lack of pressure upon the chart by the pen arm and pen itself.

Dirty Pens - If the pen appears dirty or clogged, remove it and attempt to service the tip (See Section 5.1.1.).

The pen is held on to the arm by a simple friction fit, carefully pulling it off the arm should remove most pens. If this friction fit does not separate, DO NOT FORCE the mechanism. Apply a liberal amount of deionized water or alcohol to the pen area and attempt to wash off the dried ink which may be causing the pen to stick to the arm.

After removing the pen, immerse it in a small beaker or cup full of deionized water or alcohol. Using a straight pin, single-edged razor blade, etc., attempt to remove any accumulated material from the end of the pen. Scrub the pen with a small brush prior to reinstalling. In an emergency a tightly bound piece of paper can be pulled through the pen nib. This sometimes removes the accumulating material which is causing the clog.

It is suggested that sites consider acquiring one or two extra pens from the manufacturer. Pens sometimes wear out and can be cantankerous. Sometimes the only alternative is to replace them.

Lack of Pressure - In order for the pens to write legibly upon the chart the pen and arm must contact the chart with sufficient pressure.

If the pressure on your pens is not sufficient you may notice that they seem to "float down" onto the chart drum after the pen shifter (8) is pushed back instead of dropping toward it briskly. This is likely to cause the trace to be very faint or erratic during the week.

In order to increase this pressure the pen arm stud (14) must be adjusted. First the screw on the top of the stud must be loosened and the stud rotated counterclockwise (SO AS TO MOVE THE TOP OF THE PEN ARM TOWARD THE CHART). This increases the angle with which the pen arm falls, thus increasing the pressure on the pen tip.

Clock Function - As the pen delivers ink the clock turns the chart drum and chart in a clockwise direction. This creates the X, Y axis marking familiar to us all. There are two general types of clocks available for this rain gage: 1) battery powered, and 2) wind-up clocks. Both the battery powered clocks and wind-up clocks are subject to several problems. Maintenance of the internal mechanism of both designs requires professional assistance. Local clock repair personnel may attempt repairs. Repair at the factory is also available but, generally requires a long time to complete.

Problems break down into three main categories; 1) operator error, 2) dirty or worn gear clusters, and 3) clock drive assembly malfunction.

Operator Error - The clock must be fully wound each Tuesday in order to assure a continuous record. One major benefit of electric clocks is that they don't need winding. It is suggested that winding the clock be the first step taken each time the chart drum is removed. This way it is less likely to be forgotten later.

Dirty or Worn Gear Clusters - The protocol for NADP/NTN state that each rain gage should be equipped to run an 8-day chart. In order for the chart drum to rotate at the correct speed, the drum and clock should be equipped with matching gears (25) marked 192S (see photo 5) matched to the appropriate output shaft (24).

After continuous use the gears may become worn or dirty. Typically the gears have very long lives. If they are visibly worn, then a new gear pair (one for the clock and one for the chart drum) should be ordered. Call the CAL for price and order information.

The gears can be cleaned by simply pulling them off and passing an old toothbrush or a paint brush through the teeth. A light solvent may assist in removing any hardened debris.

Clock Drive Assembly - As mentioned previously, the internal mechanism of the clock IS NOT SERVICEABLE BY SITE PERSONNEL.

The clock can be removed by simply spinning the entire clock body counterclockwise. The clock is mounted on a 1/4-inch threaded shaft.

In normal conditions the clock will run for many years without maintenance; however, when it gets dirty it will have to be cleaned and lubricated.

If the clock is subject to low temperatures during winter months a fine powdered graphite or molybdenum disulfide lubricant should be used (see Instruction Book for Universal Recording Rain Gage Cat. No. 5-780, Series/Book No. 8777 by the Belfort Instrument Co.).

5.0. Component Replacement and Routine Servicing

5.1. Component Replacement

5.1.1. Pens

Grasp the pen arm firmly with your right hand and the pen tip with your left. Gently pull the pen nib away from the arm. TRY TO REFRAIN FROM GRABBING THE PEN ON ITS RESERVOIR TIP; rather grab onto the flat section of the pen which attaches directly to the arm.

If you encounter resistance, try applying a little water to the joint between the pen and arm. Let them set for a few minutes and repeat the procedure.

As a last resort a pair of pliers may be needed to remove the pen tip. CAUTION: THE MECHANISM IS FRAGILE AND THE PEN TIP AND ARM CAN EASILY BE BENT OR BROKEN.

5.1.2. Clock

Spin the entire clock counterclockwise. It is mounted on a threaded shaft and will generally come out easily.

IF YOU HAVE AN ELECTRIC CLOCK, exercise caution not to abrade or cut the wires which lead from the clock mechanism to the battery pack.

5.1.3. Funnel

Remove the "milk can" shaped top cap of the rain gage. Rotate the funnel on the top section until the slots cut in the funnel clear the tabs in the top section. Simply pull or pry the funnel off the top section (see Photo#3).

5.2. Weekly Servicing

a. When approaching the rain gage make certain it is level and well attached to its base. Freezing and thawing over winter, animal activity, or vandalism can cause the gage to tilt. If the gage is significantly off level, measurement problems can arise.

b. Open the door to the gage.

c. Make certain the pen is in roughly the correct position. Move both the pens up and down a little to scribe an "off" tick mark. If the clock indicates a difference of more than 6 hours from the correct time, note this on the chart.

d. Lift the pens off the chart with the pen shifter and remove the drum.

e. IMMEDIATELY WIND THE RAIN GAGE CLOCK.

f. Remove the top cap of the rain gage and

    1. during the summer period dump the rain gage catch bucket, or

    2. during the winter period service the rain gage by replacing or stirring the antifreeze.

g. Reload the chart drum with a new chart and place it back on the clock mechanism. NOTE: It is suggested that sites purchase an extra chart drum (with gear). This will allow the chart to be placed on the drum in the relative calm of a truck cab or office as opposed to possibly severe conditions at the site.

h. Set the time according to the precipitation pen (NOT THE EVENT RECORDER PEN) and mark the chart with an "on" tick. Make certain the clock is ticking and the ink is flowing.

i. Close the door to the rain gage.

5.3. Other Routine Servicing Suggestions

a. Occasionally lubricate the sliding mechanism of the door with a silicon or Teflon based aerosol lubricant.

b. Once each month, after dumping the catch bucket, push the empty bucket down while watching the pens on the rain gage. Check to be certain that the event recorder and precipitation pens do not conflict and that the turnover point of the gage is still accurate. (The turnover point is the point at which the rain gage amount pen stops its upward motion and begins its downward motion.)

c. Twice each year either have the gage calibrated by a capable technician or, at a minimum, perform a simple weight or volumetric calibration check (reference Section D-4.3).

d. Twice each year check the rain gage mounting bolts and the screws attaching the housing to the mechanism base (6) for tightness.

e. An easy calibration check can be performed weekly if you have a standard 8" NWS 'STICK GAGE'. Pour the water from the Belfort catch bucket into the 2" diameter brass tube. Measure this water as normal. This measurement should be equal to the difference between the end of the Belfort gage trace and the original baseline of the trace (i.e., how much water was the Belfort weighing at the end of the week?).

f. Once each year, replace the alkaline power cells in battery powered clocks. NOTE: Sites which experience severely cold winter temperatures may require more than one battery change per year.

Condensed Operating Instructions For NADP/NTN Field Site Operation

	Procedures	Section/	Page
	Weekly Field Site Operation		
-	Take a black mailer containing a clean bucket and lid, along with a new rain gage chart and ink marker to the site.	3.2.1./	3-2
-	Remove the 'old' sample bucket from the collector at 0900 hrs. Log critical information on the bucket lid, bag and tie the bucket, then secure the bucket in the mailer for transport to the field laboratory.	3.2.2./	3-2
-	Perform checks on collector functions and CHECK THE SENSOR HEATER AFTER THE COLLECTOR HAS BEEN OPEN FOR APPROXIMATELY 5 MINUTES.	3.2.2./	3-2
-	Install a 'new', sample bucket on the collector.	3.2.2./	3-3
-	Install a new chart on the recording rain gage, then check the rain gage functions.	3.2.5./	3-5
	Field Laboratory Operations		
-	Remove the 'old' bucket from the mailer. Document any spillage. Weigh the bucket to determine if conductance and pH measurements will be made. If the weight is more than 70*gms* withdraw one 20*mL* aliquot.	3.3.1./	3-9
-	Hammer the lid on the bucket. Bag the bucket and store it in the mailer until you are ready to ship it to CAL.	3.4. /	3-19
-	Calibrate the conductance meter, measure the check solution and the precipitation sample aliquot.	3.3.4./	3-16
-	Calibrate the pH meter, measure the check solution and the precipitation sample aliquot.	3.3.4./	3-17
-	Secure conductance probe, pH electrode and buffers, standards and check solutions for storage. Discard all used solutions and vials.	3.3.4./	3-18
	Completion of the Field Observer Report Form		
-	IF bucket DOES NOT contain liquid, complete **Blocks** 1-5, 8 and 10-11). (If you perform laboratory standardization steps as recommended additionally complete **Block** 9.	3.3. /	3-6
-	If bucket contains liquid complete all **Blocks**.	3.3. /	3-6
-	Review the FORF to assure that all required information is complete and consistent.		
	Sample Shipment		
-	*Within 48 hours*, include rain gage chart and white and yellow copies of the FORF with bagged bucket. BE CERTAIN lid is secured to the bucket. Attach all four straps on mailer, turn the mailing card to reveal CAL's address and ship to CAL.	3.4. /	3-19

SECTION 9

A Discussion of Alternate Ways For Determining Site Representativeness prepared by *D.S. Bigelow* for the Unified Deposition Data Base Committee

December 11, 1987

At our last meeting, a proposal was made to modify the UDDC criteria for identifying regionally unrepresentative sites. The proposal focused on two perceived deficiencies in the current criteria: 1) that criteria was not unique to the pollutant being studied, and 2) that regional siting criteria was not independent of 'emission growth'. Out of this discussion came a third concern, that unique features about a site may render it inappropriate for use in certain types of studies or evaluations (as in our case modeling). Since the original concerns were not resolved at our last meeting they are presented again, briefly, along with a new discussion of the uniqueness issue.

Current UDDC Criteria

Presently there are seven criteria used by the Unified Deposition Data Base Committee (UDDBC) to evaluate monitoring site representativeness. The seven criteria are listed below grouped by their area of influence.

REGIONAL REQUIREMENTS

1. There Is A Continuous Industrial Source, A Town Or Suburban Area Located Within 10 Kilometers.
2. There Is A Major Point Source (>10,000 tons SO_x or NO_x per year) Located Within 50 Kilometers; Or The Sum Of Point Source Emissions Within 50 Kilometers Is Greater Than 10,000 Tons Per Year.

LOCAL REQUIREMENTS

3. There Is Surface Pollutant Storage Facilities (e.g. salt pile) Located Within 1 Kilometer.
4. There Are Major Transportation Sources, Furnaces, or Incinerators Located Within 100 Meters.
5. There is Cultivation Or Other Intensive Agricultural Activity Within 500 Meters.

ON SITE REQUIREMENTS

6. Buildings, Trees, etc, Impinge On The Cone Defined By A 30 Degree Angle Above The Horizontal Plane And Centered At The Site.
7. The Local Area Is Known To Be Dusty Due To Poor Ground Cover.

Criteria is Not Specific to Emission Type

Using the NADP/NTN sites as an example, the proposal showed that 11 sites who met the NOx limits were eliminated from Class 1 because they exceed the SOx limit, and, 5 sites who met SOx limits were eliminated because they exceed the NOx limit.

> *The main points made against making criteria specific to the pollutant of interest seem to be associated with the problem of implementation and the belief that pollutants are not independent of one another. The failure of a site to meet any single pollutant's level may in fact be an indicator of other non-rated emission problems which would make the site unrepresentative.*

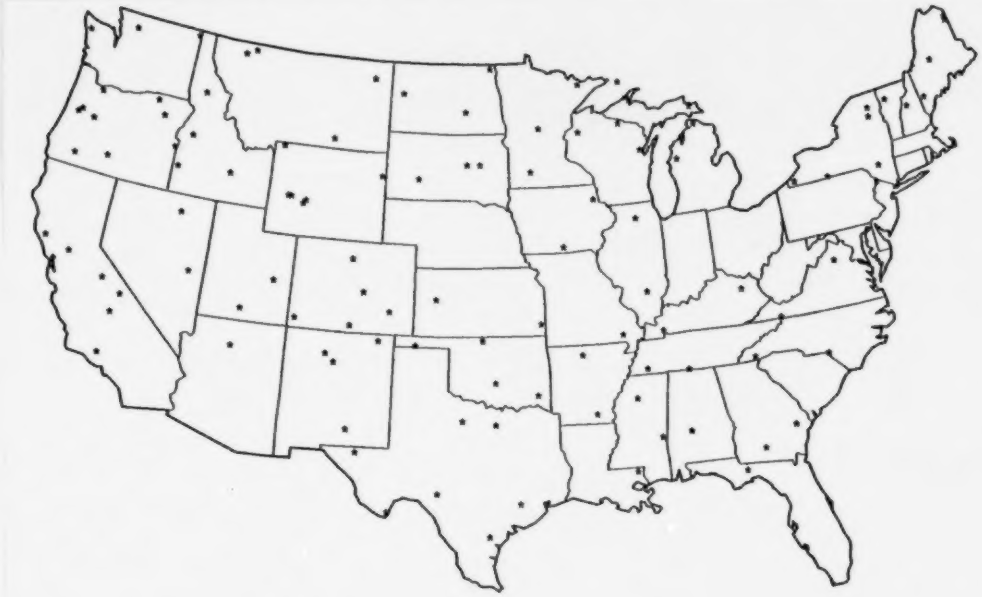
Criteria is Not Independent of Emission Growth

The current criterion indicates that either SOx or NOx emissions exceeding the 10,000 ton limit will eliminate a site from a Class 1a Site Representativeness rating. A map of sites meeting the Class 1 limits (Figure 1) show a distinct lack of sites in the Ohio river valley region. Since, on the average, emissions in this area far exceed the 10,000 emission limits, it would seem that the criteria supports the premise that there can be no background sites in high emission areas. Further as time goes on and emissions increase, more and more sites become regionally *unrepresentative*. Conversely, if emissions decrease, more sites become available. In other words the site pool is constantly changing with emissions.

The criteria could be made more *independent* of emission growth if the SOx and NOx limits were tied to the 'regional' levels. The proposal suggested that sites qualify for level 1 if the emissions at the site were less than either a) 10,000 tons/50km/ year or b) no more than one third of the regional emission average.

> ***The definition of a region and the misuse of data from the various sources the author chose to use to illustrate his point seem to be the main criticism to the proposal.***

Figure 1. USA Sites Currently Passing Both SOx and NOx Emission Criteria



Criteria Does Not Address Unique Factors At a Site Which Make The Site Unsuitable For The Data Analysis

Discussions at our last meeting and comments by Terry Clark, in his March 5, 1987 letter to Maris, reminded us that the current UDDC criteria for identifying regionally non-representative sites uses only emissions as the regional discriminator. There are, however, other features besides emissions that characterize a site and could *potentially* distinguish the site from others in it's region. Any one of these distinct features could potentially render the site unrepresentative for modeling purposes.

Table 1 lists some distinct siting features that might identify a site as unique and therefore not regionally representative. The features include emission, physiographic and meteorologic aspects of siting monitoring stations.

Emission-based characteristics include amount of material, type of source and distance from the site. Most classifications using emissions, such as our own criteria, utilize finite amounts and distances to identify unrepresentative emission receptor sites. The type of source, such as natural, area, point or short or long-range dominant is rarely included in the classification -primarily due to a lack of apportioning information. Hopefully, more recent and more complete emission inventories along with methods to classify long-range vs short-range dominant sources will allow emission based-criteria to be refined. Because of this present lack of information -especially in the identification of emissions less than 1000/tons per annum and in long-range vs short-range source identification- we must continue to rely on consensus amount and distance cut off levels.

Physiographic features are based upon classification systems first introduced by Köppen (1900, 1918, 1923, 1931), and later refined by Thornthwaite (1931), Trewartha (1943, 1967), Küchler (1964, 1973), Hammond (1964) and Bailey (1978). Since the systems are based upon the homogeneity of natural features, they are probably most effective as regional discriminators in land-based studies such as aquatic or terrestrial effects studies. Regions in these systems can be thought of as plots and each site as an observation. Emissions, rain fall and all other inputs to the region, including seasonality, constitute treatments. Robertson and Wilson (1985) used a land-based classification system (the Ecoregion) to design the NTN deposition monitoring network. Non-representative sites would be identified as ones where the site's assigned Province or Section represents an insignificant amount of Domain or Division area.

Table 1 Unique Siting Characteristics That Potentially Alter Site Representativeness

Category	Feature
Emissions:	
	point sources
	area sources
	natural sources
	proximity to population centers
	population density
	land Use
	long vs short range dominant sources
Ecoregions:	
	elevation
	slope
	seasonal precipitation
	temperature
	vegetation
	soils
	geology
Meteorology:	
	wind speeds
	temperature extremes
	variability in amount of precipitation
	precipitation type and frequency
	storm type, direction and frequency
	orographic effects
	proximity to water

Meteorologic features, some of which overlap directly or indirectly into the other classification systems, appear to be the most difficult to classify into a regional grouping. The synoptic, meso- and microscales typically used by meteorologists to study atmospheric phenomena have strong directional, diurnal and seasonal variability which often makes spatial averaging inappropriate. The meteorologic representativeness of a station is usually determined posteriori and is highly data and study specific. Statistical correlation techniques have been used by Patrinos, et. al. (1979) and Huff (1969, 1971) to illustrate spatial representativeness of precipitation under various meteorologic conditions. Nappo et al. (1981) have offered a general definition of and equation for determining the representativeness of meteorological measurements. Specific types of representativeness issues and the application of the equation were illustrated in a 1983 workshop (Nappo, 1983).

Based upon the above it seems that the committee should consider defining regional criteria in terms of three -not one- regional discriminators. These would be Emissions, Ecoregions and Meteorology. The implementation of each type of criteria category at the regional level would depend upon the study to be undertaken. Data users could declare the type and cut-off level for each criteria as appropriate for their application. The UDDC would endorse a particular combination for modeling.

Regional Emission criteria would continue to be implemented as allowable amounts within a specified distance of a site. The source of emission data (point vs area, etc) and totals by distance (at 10 km intervals for instance) could be made available to the data user via the ADDS system. Users could specify source type and distance requirements for their particular study. This would make regional emission data available in much the same way as our current completeness data. The data would be only as good as the emission inventory used. For modeling purposes we could continue to use the current criteria (10,000 tons at 50 km) but would acknowledge the subjectivity of our cut-off limits and allow others to utilize other limits.

Regional Ecoregion criteria would require the addition of ecoregion labeling to the site files in the ADDS data system. Limits could be set requiring a site's ecoregion to be above some minimum area in order for the site to be considered representative for modeling purposes. Other investigators could choose a different cut-off to suit their needs.

Meteorological criteria for regional representativeness should not be implemented a priori. However, the Committee can recommend that a posteriori examination of available meteorological observations be made when the application using unified data relies heavily on meteorologic homogeneity. The equation of Nappo and others could be cited as examples.

Selected References

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SECTION 10
Quality Assurance Report for Deposition Monitoring: Laboratory Operations 1984-1985

QUALITY ASSURANCE REPORT
NADP/NTN DEPOSITION MONITORING

Laboratory Operations
Central Analytical Laboratory
January 1984 through December 1985

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ACKNOWLEDGEMENTS

This Quality Assurance Report was prepared under the general direction of Mark E. Peden, Laboratory Manager for The Central Analytical Laboratory (CAL) of the National Atmospheric Deposition Program (NADP)/National Trends Network (NTN). The analytical data summarized in this report were produced by the laboratory personnel listed in Section II. Most of the figures were prepared by the Support Services Unit of the Illinois State Water Survey. The statistical analyses, computer generated plots and network histories were prepared by Peg A. Folta. I wish to thank Lacie L. Jeffers for the secretarial support she provided during the preparation of this report. I also want to thank Richard G. Semonin, Chief of the Illinois State Water Survey, and Gary J. Stensland, the CAL Director, for their continued support during my years at the CAL. A special note of appreciation is extended to Gail Taylor of the Illinois State Water Survey for her careful and thorough editing. Recommendations made by NADP Subcommittee 2 have been influential in the development of the overall quality assessment program at the CAL and we gratefully acknowledge the continuing support of its members. The final note of thanks goes to David Bigelow, NADP/NTN Quality Assurance Manger; Sue Bachman of the CAL staff; Kenni James, CAL Laboratory Quality Assurance Specialist; Don Bogen, Chairman of NADP/NTN Quality Assurance Steering Committee; Jerry Aubertin, Chairman of NADP/NTN Subcommittee 2; and Mary Ann Allan, Margi Böhm, Terry Dana, Cary Eaton, Ed Klappenbach, Bernie Malo, and LeRoy Schroder, members of NADP/NTN Subcommittee 2, whose assistance as reviewers resulted in this document.

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I. INTRODUCTION

The Quality Assurance Report for the Central Analytical Laboratory (CAL) of the National Atmospheric Deposition Program (NADP)/National Trends Network (NTN) for the years 1978 through 1983 was published in May 1987 (1). That report detailed the early development of the laboratory quality assurance program. This report continues the documentation of that program as it was expanded and refined in 1984 and 1985.

This report follows the format established in the report for 1978-1983. Section II documents the changes that occurred in the analytical methodology being used, in the laboratory staff, and in the laboratory facilities from January 1984 through December 1985. This is followed by the laboratory blank data (Section III). These data again resulted from the analyses of bucket leachates, filter leachates, and deionized water, providing the information necessary for assessing the potential contribution of sample collection and processing to the analyte concentrations found in the network samples. Quality control check sample (QCS) analyses continued to be utilized to quantify analytical bias and precision (Section IV). An internal blind program (Section IV) was introduced to provide another means of determining analytical bias and precision. Additional estimates of precision are achieved through replicate sample analyses (Section IV). The validity of these bias and precision estimates continues to be supported by the performance of the CAL in external quality assurance audits and interlaboratory testing programs (Section VI). Section V again details the criteria used to select samples for reanalysis and presents a discussion of the changes to the data that may result from this reanalysis process. Finally, an assessment of the performance of the CAL during 1984 and 1985 in following the guidelines set forth in the 1984 QA Plan is presented in the summary (Section VII).

In both 1984 and 1985, the laboratory was visited by members of the NADP Quality Assurance Steering Committee. The members of this committee, in conjunction with NADP Subcommittee 2 on Methods Development and Quality Assurance, advised the CAL on quality assurance (QA) program changes they felt would enhance the still developing program. By the end of 1984, the QA Steering Committee had produced the NADP Quality Assurance Plan (2), which provided formal guidelines for the laboratory quality assurance program.

II. LABORATORY QUALITY ASSURANCE PROGRAM

A. GENERAL DESCRIPTION

During 1984 and 1985 there were several changes at the CAL which affected the laboratory quality assurance program. These included the development of a methods manual for the analysis of precipitation (3); a change in the method used for the analysis of sulfate, nitrate, and chloride in precipitation samples in May 1985; and a move to new laboratory facilities in November 1985. This section addresses those changes and their impacts on the QA program. During this period, an internal blind sample submission procedure was developed, and changes were made to the existing procedures for replicate analyses. These changes are discussed in Section IV.

1. Analytical Methods Manual

Development of the analytical methods manual was made possible through funding from the U.S. Environmental Protection Agency. The laboratory manager and his staff at the Illinois State Water Survey were solely responsible for the resultant volumes. The manual provides complete procedures to be used for the analysis of precipitation samples. Included within Volume 1 are the procedures used by the CAL to determine analyte concentrations for the 11 parameters routinely analyzed in precipitation samples collected at NADP/NTN sites. Each method includes recommended quality control procedures specific to that method.

During the development of this manual, the U.S. Environmental Protection Agency requested that the method detection limits (MDL) for each method described be calculated according to the formula derived by Glaser et al. (4). This formula, which can be found in the Glossary (Appendix A), uses the standard deviation of repeated measurements of a solution containing the analyte at a concentration near the expected MDL, rather than repeated analyses of a blank sample. The formula was first used to calculate the MDLs in 1985. The publication of this manual in March 1986 provided documented standard operating procedures (SOP) for the analytical methods in use at the CAL. With the addition of this and previously published quality assurance reports detailing the QA procedures in the laboratory, SOPs for the entire laboratory operation are now available.

2. Anion Analysis by Ion Chromatography

Until May 1985, the concentrations of sulfate, nitrate, and chloride in the network samples were measured by using automated wet chemical techniques. Before requesting approval from the NADP Technical Committee for the change to analysis of these three anions by ion chromatography (IC), the CAL undertook a methods comparison study to confirm the belief that the two methods produced comparable results. A detailed account of this methods comparison was prepared by Bachman (5) and the information presented to NADP Subcommittee 2 in November 1984.

The Subcommittee found that the differences between the data from the two methods was minimal and unimportant and recommended that the full Technical Committee approve the change as requested by the CAL. Approval by the full Technical Committee for the change in methods was also given in November 1984.

As part of the comparison, 200 randomly selected precipitation samples were analyzed by both methods and the resulting analytical values compared. The plots in Figures II-1, II-2, and II-3 present the concentration ranges for sulfate, nitrate, and chloride, respectively. These plots also indicate how well the two methods compared at the different concentrations. Additionally, ten randomly selected precipitation samples were spiked with specified amounts of solutions containing known concentrations of the three anions. These spiked samples were analyzed and the percent recovery of the spiking solution calculated. Figure II-4 is a bar graph of the results from this comparison. The solutions used to spike the precipitation samples were labeled A for a solution containing low levels of the three analytes and B for one containing high levels. Results from the analysis by automated wet chemical methods are shown by the bars shaded with dots, and those resulting from analysis by IC are shown by the bars with the diagonal lines.

The plots in Figures II-1 through II-4 indicate that the data produced by the two methods for the analysis of both spiked and natural precipitation samples were comparable. Analysis using a paired t-test indicated a neglible, but statistically significant, difference at the 95% confidence interval between the data produced by the two methods. The median concentration differences for all three anions were 0.05 mg/L or less.

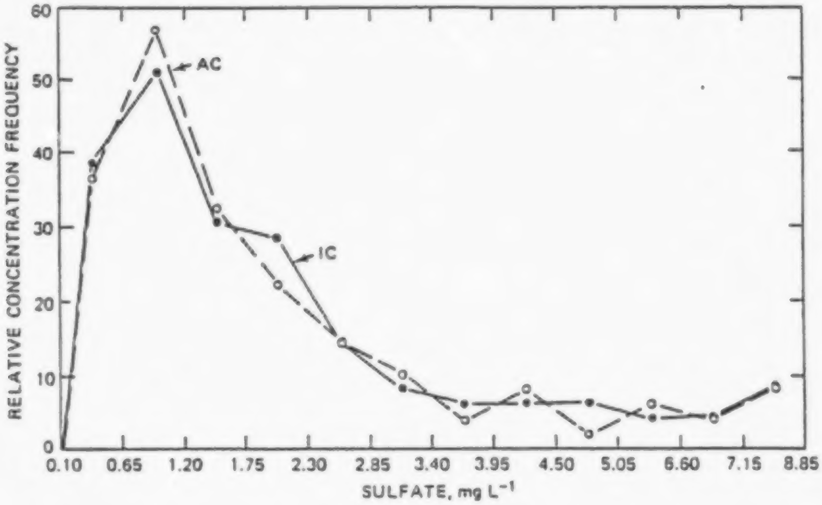

FIGURE II-1. **Comparison of the data from the analysis of the same precipitation sample by automated wet chemical methods (AC) and ion chromatograpy (IC) for sulfate.**

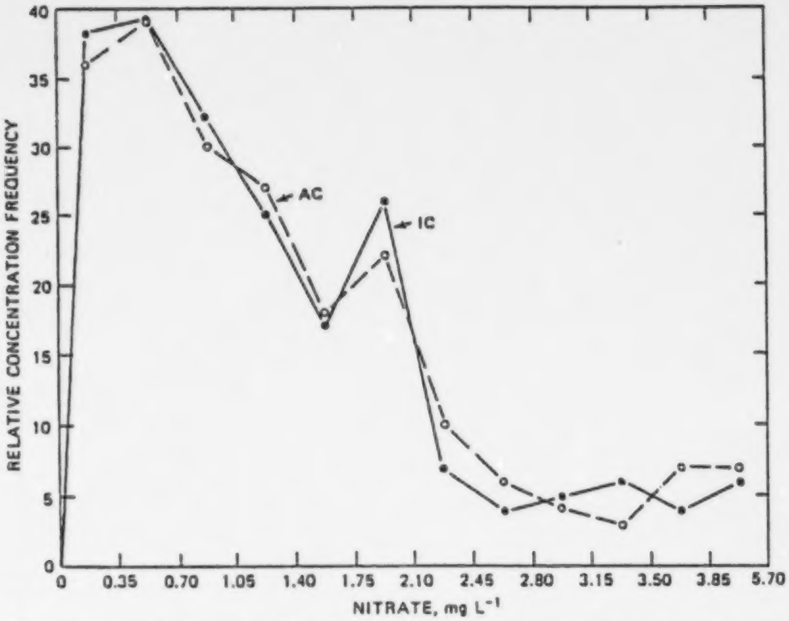

FIGURE II-2. Comparison of the data from the analysis of the same precipitation sample by automated wet chemical methods (AC) and ion chromatograpy (IC) for nitrate.

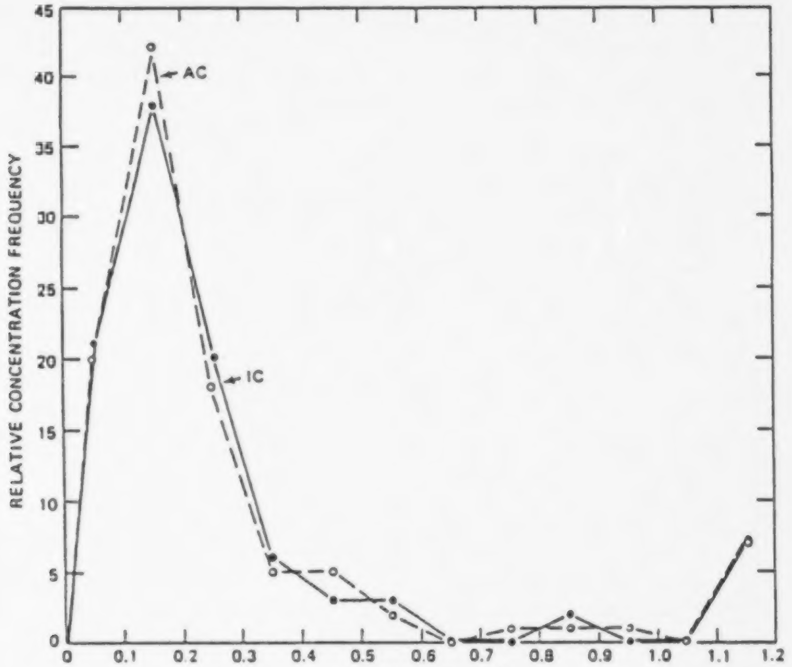

FIGURE II-3. Comparison of the data from the analysis of the same precipitation sample by automated wet chemical methods (AC) and ion chromatograpy (IC) for chloride.

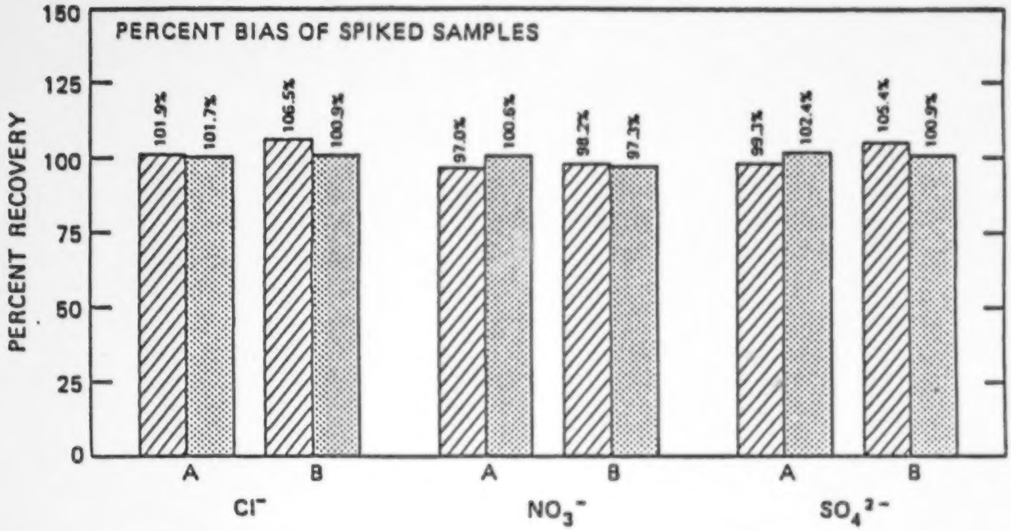

FIGURE II-4. Comparison of the percent recovery data for spiked precipitation sample analyses by ion chromatography (diagonally striped bars) and automated wet chemical methods (dotted bars). Spiking solutions approximated the 25th (A) and 75th (B) percentile concentration levels of each analyte.

The CAL requested this methods change for several reasons. The automated wet chemical methods were always susceptible to interferences from other ions that are sometimes present in precipitation. The wet chemical (AC) method used to determine the chloride content in precipitation samples measured the total concentration of all halogens present in the sample. This could lead to the reporting of chloride concentrations greater than those actually occurring in the sample. While nitrate was always the ion whose concentration was reported, the cadmium reduction method used to determine that value converted all nitrate ions found in the precipitation sample to nitrite ions. The resulting total nitrite ion concentration of the sample was then measured and reported as nitrate ion. Again, anomalous results would be reported whenever the sample contained measureable nitrite as well as nitrate. The principal interference in the sulfate determination was orthophosphate, which when present was measured as sulfate. By changing to analysis by IC these interferences were eliminated. In the IC method, each ion is eluted at a different rate and the ion concentrations are represented as discrete peaks on the chromatogram.

The other reasons for the requested change in methods included safety and economic considerations. Some of the reagents needed for the automated wet chemical methods were often hazardous and expensive. Some were unstable and had to be prepared frequently. All were used in large quantities. With the change to IC, reagent preparation time decreased significantly. The reagent chemicals needed are inexpensive and safe, and the quantities needed are smaller than those required by the wet chemical methods. These factors coupled with the increased sensitivity of the method made the change to analysis by IC very desirable and prompted the request.

The different instrumentation also resulted in different method detection limits (MDL). These increased slightly for the nitrate and chloride analyses, and decreased significantly for sulfate. Table II-1 lists the MDLs for 1984 and 1985 for all of the analytes routinely measured in precipitation samples. These new MDLs also reflect the new method of MDL calculation based on the formula used by Glaser et al. (4). The values listed in Table II-1 show that this new method for determining the MDL resulted in the same MDLs for all analytes in 1985 as in 1984. The differences seen in the MDLs for sulfate, nitrate, and chloride were due to the difference in instrument sensitivity. Finally, Figure II-5 is a sample processing flowchart for January 1981 through April 1985. With the change to analysis by IC in May, the flowchart became that depicted in Figure II-6.

TABLE II-1 Method Detection Limits for the Analysis of Precipitation Samples for 1984 and 1985.

Analyte	Method[a]	Method Detection Limit (MDL) (mg/L)	Dates
Calcium	Flame Atomic Absorption	0.009	1/84 - 12/85
Magnesium	Flame Atomic Absorption	0.003	1/84 - 12/85
Sodium	Flame Atomic Absorption	0.003	1/84 - 12/85
Potassium	Flame Atomic Absorption	0.003	1/84 - 12/85
Ammonium	Automated Phenate, Colorimetric	0.02	1/84 - 12/85
Sulfate	Automated Methyl Thymol Blue, Colorimetric	0.10	1/84 - 5/85
	Ion Chromatography	0.03	5/85 - 12/85
Nitrate-Nitrite	Automated Cadmium Reduction, Colorimetric	0.02	1/84 - 5/85
Nitrate	Ion Chromatography	0.03	5/85 - 12/85
Chloride	Automated Ferricyanide, Colorimetric	0.02	1/84 - 5/85
	Ion Chromatography	0.03	5/85 - 12/85
Ortho-phosphate	Automated Ascorbic Acid, Colorimetric	0.003	1/84 - 12/85

[a] For a complete method description, see Development of Standard Methods for the Collection and Analysis of Precipitation (3).

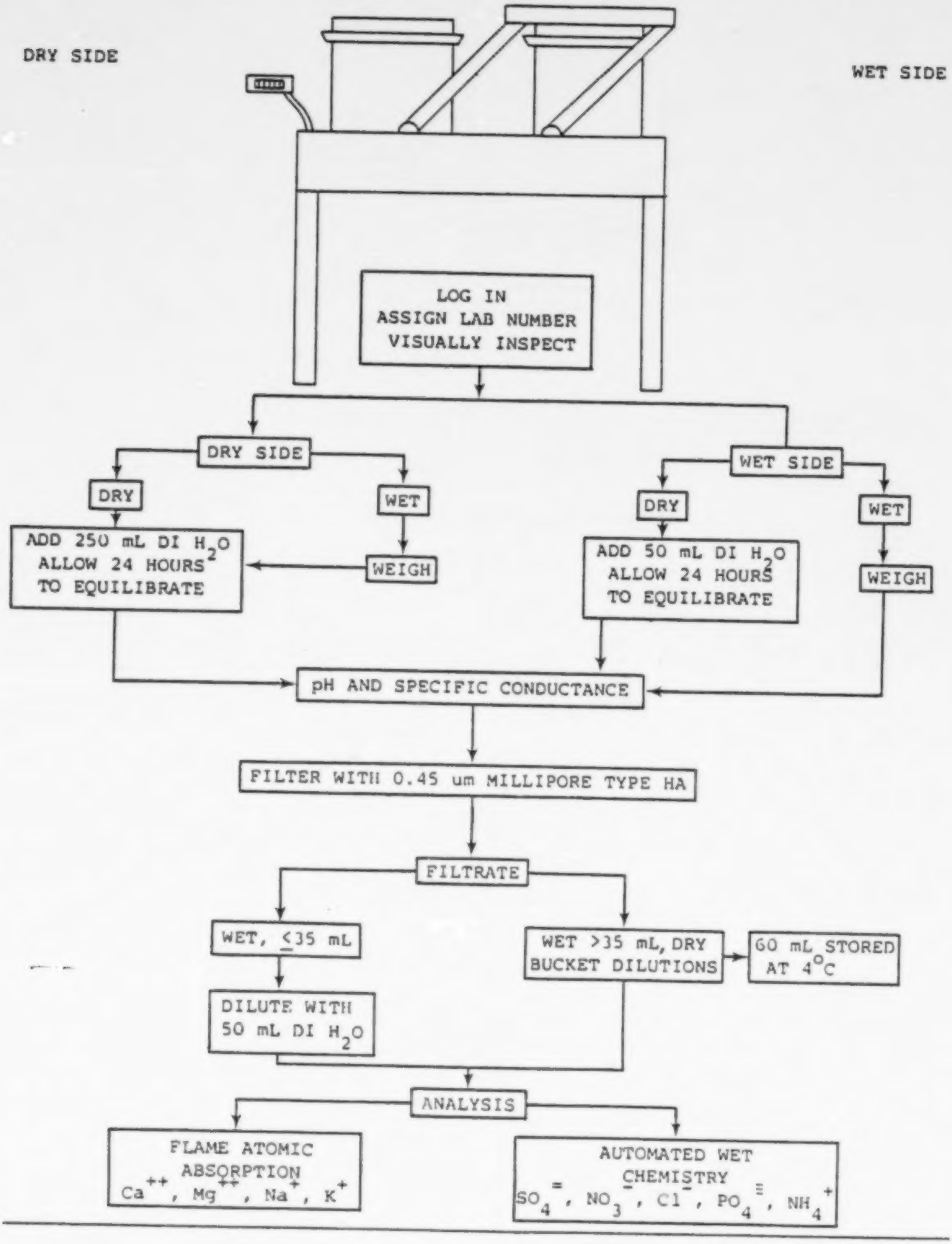
DRY SIDE
WET SIDE
LOG IN
ASSIGN LAB NUMBER
VISUALLY INSPECT
DRY SIDE
DRY
WET
ADD 250 mL DI H2O ALLOW 24 HOURS TO EQUILIBRATE
WEIGH
WET SIDE
DRY
WET
ADD 50 mL DI H2O ALLOW 24 HOURS TO EQUILIBRATE
WEIGH
pH AND SPECIFIC CONDUCTANCE
FILTER WITH 0.45 um MILLIPORE TYPE HA
FILTRATE
WET, ≤35 mL
WET >35 mL, DRY BUCKET DILUTIONS
60 mL STORED AT 4°C
DILUTE WITH 50 mL DI H2O
ANALYSIS
FLAME ATOMIC ABSORPTION
Ca++, Mg++, Na+, K+
AUTOMATED WET CHEMISTRY
SO4=, NO3−, Cl−, PO4≡, NH4+

FIGURE II-5. Sample processing flowchart for January 1981 through April 1985.

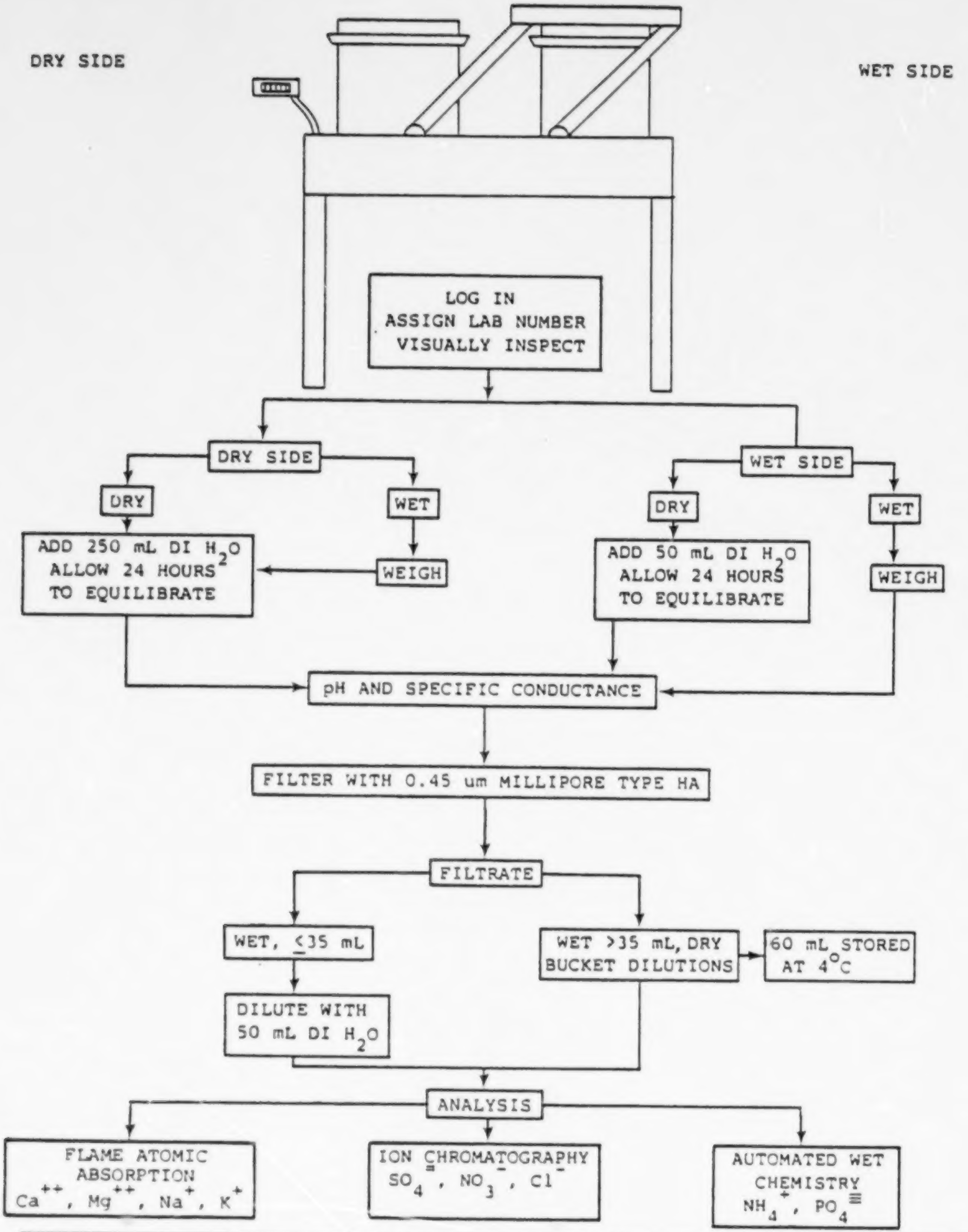
DRY SIDE
WET SIDE
LOG IN
ASSIGN LAB NUMBER
VISUALLY INSPECT
DRY SIDE
DRY
WET
ADD 250 mL DI H_2O
ALLOW 24 HOURS
TO EQUILIBRATE
WEIGH
WET SIDE
DRY
WET
ADD 50 mL DI H_2O
ALLOW 24 HOURS
TO EQUILIBRATE
WEIGH
pH AND SPECIFIC CONDUCTANCE
FILTER WITH 0.45 um MILLIPORE TYPE HA
FILTRATE
WET, ≤35 mL
WET >35 mL, DRY
BUCKET DILUTIONS
60 mL STORED
AT 4°C
DILUTE WITH
50 mL DI H_2O
ANALYSIS
FLAME ATOMIC
ABSORPTION
Ca^{++}, Mg^{++}, Na^+, K^+
ION CHROMATOGRAPHY
$SO_4^=$, NO_3^-, Cl^-
AUTOMATED WET
CHEMISTRY
NH_4^+, $PO_4^{\equiv}$

FIGURE II-6. Sample processing flowchart for May 1985 through December 1985.

3. New Facilities

The move to newly renovated facilities in November 1985 provided larger laboratories, a designated area for storage of supplies, and walk-in coolers for sample storage. The laboratory space not only increased, but also improved. Each analyst was consulted as to the design of his/her laboratory, and their suggestions were used to create large work areas that provided easy access to the instrumentation for servicing.

Laminar flow clean air workstations were installed for use in sample processing and preparation to eliminate the possible introduction of airborne contaminants into the samples. Introduction of external sources of contaminant gases and particulates was further eliminated by the positive pressure environment maintained in each laboratory and an extensive laboratory air filtration system. Disposable tacky floor mats were placed at the entrance of each laboratory to help reduce particulate loading. Two large walk-in coolers provide ample space for refrigerated storage of archival samples as well as site and laboratory supplies such as pH buffers and standard solutions.

A new reverse osmosis (RO) deionizing water system, capable of producing 500 L of deionized water with a specific conductance of <1 uS/cm, daily was installed. Wall-mounted Barnstead Nanopure systems located in each laboratory continued to be used in conjunction with point of use 0.2 um filters. Finally, the laboratory and office areas were separated for most analysts.

B. DATA AVAILABILITY

The data presented in this report have been verified by either a double entry procedure or a visual check. The data have been stored in the CAL data base and are available upon request from the CAL Director.

C. LABORATORY PERSONNEL

All of the analysts who were on the CAL staff in December 1983 remained during 1984 and 1985. Additional personnel were hired to accommodate the increasing shipping and receiving demands created by the network expansion. The only job reassignments were the result of the change in methods that occurred in 1985. The staff continued their educational development by attending manufacturers' training courses and workshops whenever possible. Table II-2 alphabetically lists the laboratory personnel who participated in the project during 1984 and 1985. It also includes a brief description of each staff member's primary function within the program and shows the duration of his/her employment as part of the CAL.

TABLE II-2 Central Analytical Laboratory (CAL) Personnel Summary (1984-1985) - Analytical Staff Only.

	Period of Service																							
Staff Member/ Job Function (month, year)[a]	1984												1985											
	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S	O	N	D
Beth Allhands Sample Receipt and Processing (Februaury, 1984)		—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Sue Bachman Ion Chromatography (August, 1980)	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Brigita Demir NH_4, NO_3, Cl	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—								
SO_4, NO_3, Cl (September, 1981)																	—	—	—	—	—	—	—	—
Pat Dodson Sample Processing (September, 1980)	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Clarence Dunbar Sample Receipt and Processing (July, 1981)	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Theresa Eckstein Sample Receipt (March, 1985)																—	—	—	—	—	—	—	—	—
Jacqueline Lockard Quality Assurance (October, 1982)	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Mark Peden Laboratory Manager (July, 1978)	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Jackie Sauer Sample Processing, pH, Specific Conductance (September, 1983)	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Loretta Skowron Ca, Mg, Na, K (July, 1978)	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Mike Slater SO_4, PO_4	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—								
NH_4, PO_4 (September, 1979)																	—	—	—	—	—	—	—	—

---

a. Date started with the CAL

III. LABORATORY BLANK DATA

The data presented in this section were generated from analyses of the deionized (DI) water used by the laboratory, DI water left in a clean sample collection bucket for 24 hours, and DI water that had been filtered through a preleached 0.45 um Millipore (HAWP) filter. All the data obtained were used to define the potential contributions of the collection vessel and the sample processing procedures to the measured analyte concentrations in precipitation. The procedures used to obtain each blank sample type are described in the NADP/NTN Quality Assurance Report for 1978-1983 (1). The resultant analytical data are presented as graphs or in tables.

A. BUCKET LEACHATES

Since May 1982, the high density polyethylene sampling buckets used in the program have been cleaned in a commercial dishwasher. The wash cycle originally used city tap water with three deionized water rinses. In November 1984 the system was changed to use only deionized water for all cycles, both wash and rinse. To determine the contribution the container might make to the analyte concentrations, clean buckets and lids were randomly selected and used to establish container blanks. Either a 50 mL, 150 mL, or 500 mL portion of deionized water was poured into the test bucket, the lid was pounded on, and the water was left to equilibrate in the bucket. Three test buckets, each containing a different volume of DI, were inverted during this period of equilibration, and another three were allowed to remain in an upright position. After 24 hours, these bucket leachates were poured into DI water-washed 60 mL polyethylene (LPE) bottles and the concentration of analytes was determined. Figures 1 through 20 in Appendix B are plots of the analyte masses measured in these bucket blanks for 1984 and 1985.

For all volumes of all types of bucket blanks, the measured orthophosphate concentrations were at or below the method detection limit; therefore, plots of orthophosphate masses are not included. The concentrations of the measured analytes have been converted to micrograms per bucket in order to place the data for all three volumes on the same plot. Mass per bucket is calculated by multiplying the analyte concentration in units of micrograms per milliliter by the sample volume in milliliters. A legend defining the symbols being used is presented with each series of analyte plots. The dashed line near the bottom of each plot represents the minimum detectable mass for that analyte. This minimum value was determined by multiplying the MDL, expressed as micrograms per milliliter, by 50 mLs. For all three volumes, values measured as less than the method detection limit were plotted on this line. Table 1 in Appendix B lists the MDL mass for all of the parameters for which there are bucket blank plots.

Table III-1 presents annual median masses again expressed as micrograms per bucket, for both inverted and upright bucket blanks analyzed in 1984 and 1985. The data document high concentrations of analytes for 1984 and very small concentrations of analytes for 1985.

The source of these differences in concentrations was traced to a clogged spray arm in the dishwasher. The city tap water used in the wash cycle, which contains high levels of calcium, magnesium, and sodium, was not being completely removed by the three DI water rinses. To correct the situation and prevent it from recurring, the entire wash cycle was converted in November 1984 to utilize deionized water only. The median values for 1985 indicate that the problem was corrected and the bucket leachates now contain very limited amounts of all of the analytes of interest.

TABLE III-1 Median Analyte Concentrations Expressed as Mass (ug)/Bucket Found in Upright and Inverted Bucket Blanks in 1984 and 1985.

	Upright		Inverted	
Analyte	**1984**	**1985**	**1984**	**1985**
Calcium	7.10	0.58	16.83	1.95
Magnesium	4.62	0.30	9.17	1.38
Sodium	9.58	0.47	20.57	1.45
Potassium	1.68	0.18	3.20	0.43
Ammonium	1.4	<1.0	1.3	<1.0
Sulfate	8.9	<1.5	24.2	3.2
Nitrate-Nitrite	<1.0	<1.5	1.5	<1.5
Chloride	4.3	<1.5	14.6	1.8
Ortho-phosphate	<0.15	<0.15	<0.15	<0.15
pH (units)	5.97	5.59	6.24	5.75
Specific Conductance (uS/cm)	2.2	1.4	3.6	1.6

In 1984, a decision was made to add the measurements of pH and specific conductance for these bucket leachates to the analysis for the other analytes. Figures 9 and 19 in Appendix B show that the pH of these samples is typically greater than pH 5.5. The expected pH for DI water in equilibrium with atmospheric CO_2 would be approximately pH 5.7. The deviation from that theoretical value is not very large and is accounted for by the presence of ions other than CO_2 in the samples. The larger the concentration of other ions, the greater the variability in the measured pH. This is clearly evident in the two plots for pH. Figures 10 and 20 in Appendix B are plots of the measured specific conductance values. The expected specific conductance would be between 1 and 2 uS/cm. For the majority of the blanks, this is the case; however, these data follow the same patterns as do the data for pH. Again, the presence of other ions in the precipitation results in specific conductance values higher than anticipated. As with the pH measurements, the higher the concentration of ions, the more variability seen in the specific conductance measurements.

Concern about the collection bucket lid gasket as a potential source of contaminants continued and prompted two special studies to investigate the problem. In the first of these studies, the leaching effect of an acidic solution on the sample container was tested. Two dilute nitric acid solutions were substituted for the DI water that was routinely used for bucket leachate tests. One of the solutions had a pH of 4.30, and the other had a pH of 4.60. The standard three sample volumes were used and the acidic solutions were allowed to equilibrate in both inverted and upright clean buckets for the usual period of 24 hours. Table III-2 gives the median analyte concentrations expressed as micrograms/bucket for these acid blanks. The calculated nitrate is 160 ug for the pH 4.30 sample and 80 ug for the pH 4.60 sample. This leachate test was performed at two different times. The test using the pH 4.60 nitric acid solution took place in late 1983. During the testing period the dishwasher problems previously discussed had already begun. Elevated levels of analytes, particularly cations, that are evident in Table III-2 were most likely due to this problem. The test using the pH 4.30 solution was performed in 1985 when routine blanks indicated that the buckets were analyte free. Keeping the testing periods in mind, the analyte concentrations for these acid bucket leachates are similar to the concentrations found in the routine bucket blanks from the same period (Table III-1).

The second study compared the data obtained from the analysis of blanks that utilized either DI water or a pH 4.30 QCS nitric acid as the leaching solutions. Again three sample volumes were used and some buckets were inverted while others remained upright. The variable being examined in this study was prolonged exposure of the bucket to the acid or the DI water. It was determined that the maximum time of travel for samples from network sites to the CAL was one week. The samples collected for this experiment remained in the buckets for one week to simulate this maximum time of contact with the container surface. All samples and buckets used for this test were prepared and analyzed in 1985. Table III-3 presents the results of this experiment. These data indicate that prolonged exposure to the bucket surface (and particularly contact with the lid gasket that occurs when the bucket is inverted) may result in increased analyte concentrations in the sample. The upright blanks, however, show that the actual risk of sample contamination from the collection container, even when there is prolonged exposure to the bucket surface, does not increase significantly with increased sample acidity.

TABLE III-2 Median Analyte Concentrations Expressed as Mass (ug)/Bucket Found in Upright and Inverted Bucket Blanks Using Dilute Nitric Acid as the Leaching Solution - One Day Equilibration.

	Upright		Inverted	
Analyte	4.30	4.60	4.30	4.60
Calcium	0.65	3.85	1.95	8.90
Magnesium	1.45	2.10	2.90	4.20
Sodium	6.50	8.00	6.05	16.90
Potassium	<0.15	6.60	1.50	17.83
Ammonium	<1.0	<1.0	<1.0	<1.0
Sulfate	<1.5	<5.0	5.5	<5.0
Nitrate-Nitrite	161.0	80.0	162.0	80.0
Chloride	<1.5	9.0	<1.5	22.5
Ortho-phosphate	<0.5	<0.15	<0.5	<0.15
pH (units)	4.35	4.79	4.41	4.89
Specific Conductance (uS/cm)	20.0	9.1	18.9	7.1

TABLE III-3 Median Analyte Concentrations Expressed as Mass (ug) /Bucket Found in Upright and Inverted Bucket Blanks Using Dilute Nitric Acid and Deionized Water as the Leaching Solutions - One Week Equilibration.

	Upright		Inverted	
Analyte	DI	4.30	DI	4.30
Calcium	<0.45	<0.45	5.50	1.75
Magnesium	<0.15	0.90	5.01	1.40
Sodium	0.45	1.50	0.80	1.35
Potassium	<0.15	<0.15	<0.15	<0.15
Ammonium	<1.0	<1.0	<1.0	<1.0
Sulfate	7.5	<1.5	10.5	<1.5
Nitrate-Nitrite	<1.5	161.0	<1.5	160.5
Chloride	<1.5	<1.5	<1.5	<1.5
Ortho-phosphate	<0.5	<0.5	<0.5	<0.5
pH (units)	5.56	4.35	6.20	4.38
Specific Conductance (uS/cm)	1.6	20.3	1.8	18.5

B. FILTER LEACHATES

Two filter leachates were collected each week during 1984 and 1985. All filters are leached before use with a 250 mL aliquot of DI water. After this leaching procedure, a 50 mL portion of DI is poured through the same filter and this time the leachate collected for analysis. This is filter leachate A. A second 50 mL portion of DI is then poured through this same filter and the leachate again collected for analysis. This second sample is leachate B. Table III-4 provides the median concentrations of the analytes found in these leachates for 1984 and 1985. More complete annual summaries of the analyses of these filter leachates can be found in Tables 2 through 6 in Appendix B. The data presented in these tables show the filters to be a negligible source of contamination. If elevated levels of analytes occur in these blank samples, it is usually in those analytes associated with human activities, namely sodium and chloride. The data do not show these increased analyte concentrations to be a constant problem, but they do appear in some degree in 50% of the A type filter leachates. The data also show that these problems disappear in the B leachates. As a result of this observation, in 1986 the CAL increased the initial leaching volume from 250 to 300 mL to further reduce the occurrence of this type of contamination. The routine weekly monitoring of these leachates continues as an integral part of the CAL quality assurance program.

TABLE III-4 Median Analyte Concentration Found in Filter Leachates A and B for 1984 and 1985.

	Median Concentration (mg/L)			
	Leachate A		Leachate B	
Analyte	1984	1985	1984	1985
Calcium	<0.009	<0.009	<0.009	<0.009
Magnesium	<0.003	<0.003	<0.003	<0.003
Sodium	0.004	0.010	<0.003	<0.003
Potassium	<0.003	<0.003	<0.003	<0.003
Ammonium	<0.02	<0.02	<0.02	<0.02
Sulfate	<0.10	<0.10 <0.03	<0.10	<0.10 <0.03
Nitrate-Nitrite	<0.02	<0.02 <0.03	<0.02	<0.02 <0.03
Chloride	<0.02	<0.02 <0.03	<0.02	<0.02 <0.03
Orthophosphate	<0.003	<0.003	<0.003	<0.003
n[a]	50	47	50	47

[a] number of analyses

C. DEIONIZED WATER

The final routine quality control check was on the quality of the deionized water used throughout the laboratory. Although the purity of the water was monitored by daily checks of specific conductance through use of an in-line conductivity meter, the complete analysis of DI water samples was begun in 1980 and continues to the present. During 1984 and 1985 weekly samples were routinely taken from both the sample processing laboratory and the atomic absorption laboratory for complete analysis. A description of the deionizing systems in use at the laboratory during 1984 and 1985 can be found in the QA Report for 1978-1983 (1) and in the discussion of the new laboratory facilities in Section II of this report.

Table III-5 lists the median analyte concentrations found in the deionized water used by the CAL in 1984 and 1985. Tables 7 through 11 in Appendix B contain more complete annual summaries of the data obtained from the analyses of this DI water. As with the filters, the laboratory deionized water has proven to be a negligible source of contamination. Analysis of deionized water used in the sample processing laboratory as well as of a DI water sample taken from one of the analytical labs at the CAL continues as part of the routine quality assessment program.

TABLE III-5 Median Analyte Concentration Values for Deionized Water Blank for 1984-1985.

	Median Concentration Value (mg/L)			
	Room 61[a]		Room 129[a]	
Analyte	1984	1985	1984	1985
Calcium	<0.009	<0.009	<0.009	<0.009
Magnesium	<0.003	<0.003	<0.003	<0.003
Sodium	<0.003	<0.003	<0.003	<0.003
Potassium	<0.003	<0.003	<0.003	<0.003
Ammonium	<0.02	<0.02	<0.02	<0.02
Sulfate	<0.10	<0.10 <0.03	<0.10	<0.10 <0.03
Nitrate-Nitrite	<0.02	<0.02 <0.03	<0.02	<0.02 <0.03
Chloride	<0.02	<0.02 <0.03	<0.02	<0.02 <0.03
Orthophosphate	<0.003	<0.003	<0.003	<0.003
n[b]	49	41	29	37

a. sample processing laboratory is room 61, and atomic absorption spectroscopy laboratory is room 129

b. number of analyses

IV. LABORATORY BIAS AND PRECISION

An essential part of every quality assurance program is the determination of the accuracy of the measurements being made by the laboratory. For the years 1984 and 1985, the CAL used data obtained from replicate analyses of Quality Control Check Samples (QCS) as one means of assessing analytical bias and precision. These QCS were either internally formulated solutions or dilutions of mineral and nutrient concentrates provided by the United States Environmental Protection Agency, EMSL-Cincinnati, Ohio. Additional information regarding laboratory precision was obtained through the analysis of replicate samples, i.e., the analysis of two aliquots of the same sample. The third means employed by the CAL for data assessment was the use of samples with known analyte concentrations that were submitted as blinds to the analysts. This section contains descriptions of the samples used by the CAL to assess laboratory performance. Summary tables and plots of the analyses of these samples are provided in this report accompanied by a discussion of what the data indicate about the performance of the Central Analytical Laboratory.

A. QUALITY CONTROL CHECK SAMPLE DATA

As was the case during the previous six-year period, the QCS used by the laboratory were internally formulated samples to monitor the pH and specific conductance measurements, and dilutions of the USEPA mineral and nutrient concentrates to monitor the remaining parameters. The laboratory diluted the EPA sample concentrates so the resulting concentration for the analyte being monitored fell near the 25th and 75th percentiles for the NADP/NTN network samples. The percentile concentration values for all the routinely analyzed precipitation parameters for the years 1984 and 1985 are given in Table IV-1 and Table IV-2.

A minimum volume of 35 mL of sample is necessary for a complete analysis of all eleven precipitation parameters. Samples containing less than 35 mL are diluted as indicated in Figures II-1 and II-2. Because of this processing procedure, only samples which were greater than 35 mL in volume have been included in the preparation of the percentile concentration tables.

During 1984 and 1985 the network continued to expand primarily westward. By the end of 1985 there were nearly 200 sites in operation throughout the country, including ones in Alaska, Hawaii, and Puerto Rico. An examination of the percentile concentration values indicates that differences in the ionic concentrations during this period occurred only for the major cations. The concentrations measured in 1984 are greater than those found in 1985. Some of these differences may have been the result of the bucket washing problem that occurred in 1984. This problem was explained in more detail in Section III of this report. The elimination of the problem is most obvious in the bucket blank plots for 1985 that are found in Appendix B.

TABLE IV-1 Percentile Concentration Values of Chemical and Physical Parameters Measured in Precipitation - 1984.

Parameter	Percentile Concentration Values (mg/L)									
	Min.	5th	10th	25th	50th	75th	90th	95th	99th	Max.
Ca	<0.009	0.030	0.050	0.080	0.170	0.380	0.760	1.20	2.82	22.8
Mg	<0.003	0.013	0.016	0.026	0.047	0.094	0.201	0.296	0.603	2.3
K	<0.003	0.008	0.010	0.017	0.030	0.061	0.125	0.186	0.447	5.8
Na	<0.003	0.027	0.035	0.059	0.118	0.269	0.625	1.05	3.14	10.8
NH_4	<0.02	<0.02	<0.02	0.08	0.19	0.40	0.69	0.95	1.62	3.5
NO_3	<0.02	0.15	0.27	0.58	1.13	1.99	3.13	4.11	6.70	27.4
Cl	<0.02	0.06	0.08	0.11	0.19	0.39	0.93	1.63	6.13	37.8
SO_4	<0.10	0.39	0.50	0.83	1.49	2.65	4.27	5.68	9.51	45.7
PO_4	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	0.006	0.009	0.013	12.6
pH (units)	2.98	4.01	4.15	4.38	4.80	5.46	6.08	6.34	6.80	7.85
Specific Conductance (uS/cm)	1.6	3.7	5.0	8.5	15.2	26.9	42.4	54.2	91.2	566.8

Source: National Atmospheric Deposition Program (NADP)
1984 - wet side samples
Number of samples = 5450

TABLE IV-2 Percentile Concentration Values of Chemical and Physical Parameters Measured in Precipitation - 1985.

Parameter	Percentile Concentration Values (mg/L)									
	Min.	5th	10th	25th	50th	75th	90th	95th	99th	Max.
Ca	<0.009	0.030	0.040	0.060	0.140	0.290	0.610	0.930	2.09	14.9
Mg	<0.003	0.010	0.014	0.021	0.037	0.071	0.135	0.200	0.416	1.4
K	<0.003	0.004	0.006	0.012	0.025	0.049	0.100	0.153	0.383	2.9
Na	<0.003	0.015	0.020	0.036	0.075	0.185	0.480	0.881	2.59	10.80
NH_4	<0.02	<0.02	<0.02	<0.02	0.16	0.37	0.65	0.92	1.79	7.4
NO_3	<0.03	<0.03	0.12	0.48	1.05	1.84	3.05	4.09	7.23	25.4
Cl	<0.03	<0.03	0.05	0.09	0.17	0.36	0.86	1.53	4.70	20.9
SO_4	<0.10	0.24	0.35	0.71	1.41	2.55	4.01	5.32	8.73	30.5
PO_4	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	0.009	0.012	0.028	2.2
pH (units)	3.38	4.03	4.14	4.37	4.76	5.30	5.89	6.25	6.73	7.7
Specific Conductance (uS/cm)	1.6	3.6	4.9	8.1	15.0	26.6	41.1	52.8	87.6	262.2

Source: National Atmospheric Deposition Program (NADP)
1985 - wet side samples
Number of samples = 6089

As the network expanded, the number of precipitation samples being collected and analyzed increased. This resulted in an increase in the number of analyses of quality control samples as well. The program grew in terms of the quantity of quality assessment data being produced but did not change in the types of samples being analyzed to produce these data. The following subsections describe the quality control solutions used by the laboratory, present summary tables of the data that resulted from their analysis, and provide an explanation of what these data imply about the performance of the CAL.

1. Solutions Used

Since 1981, a dilute nitric acid solution (5.01×10^{-5}N HNO_3) prepared by the CAL has been used to monitor pH and specific conductance measurements. The solution preparation is verified by measuring the pH and specific conductance and by analysis colorimetrically or chromatographically for NO_3 and titrimetrically for acidity. The information obtained from these determinations is used to derive the calculated pH and specific conductance values. The solution must have a calculated pH of 4.30 ± 0.03 and a calculated specific conductance of 21.8 ± 2 uS/cm to be considered suitable for use in both the laboratory and the field.

Also since 1981, a dilute potassium chloride solution (5.0×10^{-4}N KCl) formulated and prepared at the CAL has been used both to calibrate the conductivity bridge and cell and to monitor pH measurements at a second concentration level. The accuracy of this preparation is determined by measurement of pH and specific conductance, colorimetric or chromatographic determination of the chloride concentration, and analysis of the potassium concentration by flame atomic absorption spectroscopy. These analytical data are used to calculate the pH and specific conductance of the preparation. Although this is a stable solution, its calculated pH of 5.63 falls within the range of pH at which the effects of atmospheric carbon dioxide fluctuations can be significant. For that reason the range of acceptable readings for pH is 5.63 ± 0.3 pH units. The acceptable range for the calculated specific conductance is 74.8 ± 2 uS/cm.

The bias and precision of the remaining analytical parameters were monitored by performing replicate analyses of dilute QCS solutions prepared from USEPA mineral and nutrient concentrates. The mineral sample was used to prepare QCS solutions for calcium, magnesium, sodium, potassium, sulfate, and chloride. The QCS solutions for nitrate-nitrite, ammonium, and orthophosphate were made by diluting the USEPA nutrient concentrates. Two QCS solutions were prepared for each analyte. One solution approximated the 25th percentile concentration found for the specified analyte, and the other approximated the 75th.

2. Analytical Bias and Precision Tables

The formulas used to calculate the bias and precision data can be found in the Glossary (Appendix A). All data presented for the measurement of pH required the conversion of the measurements from pH units to hydrogen ion content as microequivalents per liter before these formulas could be employed. Table IV-3 lists several pH values and their corresponding hydrogen ion content. The summaries of pH data present the mean and standard deviation values in both pH units and microequivalents per liter. The percent bias and percent relative standard deviation (RSD) values are calculated by using the hydrogen ion concentration only.

TABLE IV-3 Selected pH Values and the Corresponding Hydrogen Ion Content Expressed as Microequivalents per Liter.

pH (units)	Hydrogen Ion (ueq/L)
3.50	316.2
4.00	100.0
4.30	50.1
4.50	31.6
4.70	20.0
5.00	10.0
5.30	5.0
5.50	3.2
5.70	2.0

Tables IV-4 and IV-5 were prepared from the data obtained from replicate analysis of QCS solutions. For all parameters except pH and specific conductance, at least one QCS was analyzed with each group of twelve precipitation samples. For pH and specific conductance measurements, the frequency was approximately one QCS measured for every twenty precipitation samples. The annual summaries of bias and precision for each parameter were produced by using the results obtained from the statistical analysis of these QCS data. These tables provide one means of assessing the quality of the analytical data produced at the CAL by presenting summaries of the analyses of solutions whose analyte concentrations were known to each analyst.

As mentioned before, the primary source of the QCS being analyzed was the USEPA. With each of the mineral and nutrient concentrates that it supplies, the USEPA provides directions for sample preparation plus a data sheet which lists an expected analyte concentration, a mean analyte concentration with a standard deviation, and a confidence interval for the analyte concentrations that should result after dilution. These mean and standard deviation values were obtained from statistical analysis of the data received from USEPA-sponsored interlaboratory performance studies (6). Summaries of the data obtained from these performance

TABLE IV-4 Analytical Bias and Precision for 1984 - Determined from Analysis of Quality Control Check Samples.

Parameter	Theoretical Concentration, mg/L	Measured Concentration, mg/L	n[a]	Bias		Precision		Critical	Statistically Significant Bias?[b]
				mg/L	%	s mg/L	RSD %	%	
Calcium	0.053	0.050	473	-0.003	-5.7	0.003	6.0	2.2	YES
	0.067	0.065	37	-0.002	-3.0	0.002	3.1	2.7	YES
	0.317	0.322	36	0.005	1.6	0.003	0.9	1.4	YES
	0.402	0.414	478	0.012	3.0	0.004	1.0	1.5	YES
Magnesium	0.018	0.017	474	-0.001	-5.6	0.001	5.9	3.1	YES
	0.024	0.024	37	0.000	0.0	0.001	4.2	3.8	NO
	0.070	0.070	36	0.000	0.0	0.001	1.4	2.5	NO
	0.083	0.084	473	0.001	1.2	0.001	1.2	2.0	NO
Sodium	0.071	0.071	32	0.000	0.0	0.001	1.4	1.7	NO
	0.083	0.084	467	0.001	1.2	0.002	2.4	1.7	NO
	0.395	0.403	32	0.008	2.0	0.003	0.7	1.3	YES
	0.459	0.477	468	0.018	3.9	0.004	0.8	1.3	YES
Potassium	0.017	0.017	32	0.000	0.0	0.001	5.9	3.9	NO
	0.021	0.020	466	-0.001	-4.8	0.001	5.0	2.7	YES
	0.074	0.072	33	-0.002	-2.7	0.001	1.4	2.3	YES
	0.100	0.094	465	-0.006	-6.0	0.002	2.1	2.2	YES
Ammonium	0.36	0.37	294	0.01	2.8	0.01	2.7	1.2	YES
	1.23	1.24	302	0.01	0.8	0.03	2.4	0.8	NO
Sulfate	0.92	0.91	475	-0.01	-1.1	0.08	8.8	1.6	NO
	6.86	7.30	476	0.44	6.4	0.30	4.1	4.4	YES
Nitrate	0.62	0.63	298	0.01	1.6	0.02	3.2	1.4	YES
	3.14	3.11	310	-0.03	1.0	0.07	2.3	1.3	NO
Chloride	0.86	0.87	292	0.01	1.2	0.02	2.3	0.9	YES
	1.80	1.85	291	0.05	2.8	0.03	1.6	1.4	YES
Ortho-phosphate	0.15	0.14	468	-0.01	-8.5	0.01	7.1	2.3	YES
	0.22	0.20	467	-0.02	-7.0	0.02	10.0	2.1	YES
pH units	4.30	4.32	222	0.02		0.02			
(ueq/L)	(50.1)	(48.0)		(-2.1)	-4.2	(2.4)	5.0	6.3	NO
	5.63	5.44	222	-0.19		0.05			
	(2.3)	(3.5)		(1.2)	52.2	(0.4)	11.4	58.4	NO
Specific Conductance (uS/cm)	21.8	21.0	222	-0.8	-3.7	0.6	2.9	6.3	NO

a. number of replicates

b. 95% confidence level

TABLE IV-5 Analytical Bias and Precision for 1985 - Determined from Analysis of Quality Control Check Samples.

Parameter	Theoretical Concentration, mg/L	Measured Concentration, mg/L	n[a]	Bias mg/L	Bias %	Precision s mg/L	Precision RSD %	Critical %	Statistically Significant Bias?[b]
Calcium	0.053	0.053	512	0.000	0.0	0.002	3.8	2.1	NO
	0.402	0.409	503	0.007	1.7	0.004	1.0	1.5	YES
Magnesium	0.018	0.018	537	0.000	0.0	0.001	5.6	3.1	NO
	0.083	0.083	538	0.000	0.0	0.001	1.2	2.0	NO
Sodium	0.083	0.083	485	0.000	0.0	0.001	1.2	1.7	NO
	0.459	0.475	507	0.016	3.5	0.004	0.8	1.3	YES
Potassium	0.021	0.022	489	0.002	4.8	0.002	9.1	2.8	YES
	0.100	0.094	485	-0.006	-6.0	0.002	2.1	2.2	YES
Ammonium	0.19	0.18	215	-0.01	-5.3	0.02	11.1	2.6	YES
	0.36	0.36	82	0.00	0.0	0.02	5.6	1.7	NO
	0.98	0.92	224	-0.06	-6.1	0.05	5.4	1.1	YES
	1.22	1.23	81	0.01	0.8	0.02	1.6	0.8	NO
Sulfate	0.69	0.72	340	0.03	4.4	0.03	4.2	4.4	NO
	0.92	0.92	655	0.00	0.0	0.04	4.4	1.4	NO
	3.43	3.69	122	0.26	7.6	0.11	3.0	4.4	YES
	6.86	7.13	172	0.27	3.9	0.11	1.5	4.4	NO
Nitrate	0.62	0.63	88	0.01	1.6	0.02	3.2	1.5	YES
	0.80	0.81	509	0.01	1.3	0.02	2.5	1.6	NO
	3.14	3.11	88	-0.03	1.0	0.07	2.3	1.4	NO
	3.54	3.63	438	0.09	2.5	0.13	3.6	0.8	YES
Chloride	0.18	0.18	132	0.00	0.0	0.02	11.1	2.4	NO
	0.86	0.87	584	0.01	1.2	0.03	3.5	0.9	YES
	1.80	1.87	360	0.07	3.9	0.04	2.1	1.4	YES
Ortho-phosphate	0.03	0.03	151	0.00	0.0	0.01	33.3	6.9	NO
	0.06	0.05	161	-0.01	-19.4	0.01	20.0	5.2	YES
	0.12	0.12	84	0.00	0.0	0.01	8.3	3.9	NO
	0.15	0.13	59	-0.02	-15.0	0.01	7.7	3.2	YES
	0.21	0.19	84	-0.02	-8.2	0.02	10.5	2.9	YES
	0.22	0.20	74	-0.02	-7.0	0.01	5.0	2.2	YES
pH units	4.30	4.32	248	0.02		0.02			
(ueq/L)	(50.1)	(47.3)		(-2.8)	-5.6	(3.2)	6.8	6.3	NO
	5.63	5.43	248	-0.20		0.06			
	(2.3)	(3.7)		(1.4)	60.9	(0.5)	13.5	88.4	NO
Specific Conductance (uS/cm)	21.0	21.5	248	-0.3	-1.4	0.6	2.8	6.3	NO

a. number of replicates
b. 95% confidence level

studies can be obtained from the USEPA, EMSL-Cincinnati, Ohio. In Tables IV-4 and IV-5, the USEPA mean is listed in the theoretical concentration column and is used to calculate the analytical bias values. The last column of the tables indicates whether the bias that has been calculated from the CAL data is or is not statistically significant. To determine this, a t-test was used to compare the mean values measured at the CAL to those provided by the USEPA on its data sheets. This comparison resulted in the critical percent value which is listed in Table IV-4 and Table IV-5. Whenever the calculated percent bias for a measured parameter was greater than or equal to the critical percent, that bias was considered to be statistically significant. The formula used for the calculation of the critical percent is listed in the Glossary (Appendix A).

3. Discussion of Results

A review of Tables IV-4 and IV-5 indicates few problems with analytical bias during 1984 and 1985. Although the results of the t-test show that the deviation of the CAL mean from the theoretical value (USEPA mean) was often statistically significant, the actual percent bias is <5% for 76% of the 29 measured parameters in 1984 and for 69% of the 32 measured parameters in 1985. For those parameters whose percent bias measures >5%, that greater percentage difference often represents a very small difference in the actual analyte concentration. This is particularly true when the analyte concentrations are very low, as are those that fall near the 25th percentile levels. As analyte concentrations decrease, the degree of difficulty in obtaining accurate dilutions increases. Increased variability of the analytical measurements (decreased precision) is also typically present for samples containing very small amounts of analyte.

The data presented in Table IV-4 for 1984 indicate that most of the measured parameters are statistically biased. A closer look at the actual concentrations show that the only areas where problems may really exist are with orthophosphate and pH measurements. The bias in the orthophosphate measurements is negative. This is most likely due to the instability of the orthophosphate ion. Both fresh dilutions of stock QCS and standards are prepared every three days to eliminate this problem. The data show that this procedure has been effective and that the percent bias and the percent relative standard deviation are $\leq$10%. The large bias in the pH 5.63 QCS is principally due to the allowable inaccuracy in the sample preparation. The deviation in pH units is within the desired limits ($\pm$ 0.03 pH units) for sample use. These limits were discussed earlier in this section. The bias and precision calculations, however, were performed by using the hydrogen ion concentration. The result is alarmingly large bias percentages and relative standard deviation. This pH (5.63) corresponds to only 2.3 ueq of hydrogen ion. Very small changes in the pH and the calculated hydrogen ion content will result in a very large percent bias.

In 1985, problems again occur in the orthophosphate and the pH measurements. The reasons for these deviations are the same as those to which the differences were attributed in 1984. In 1985 the concentration of the orthophosphate QCS was lowered to better simulate the analyte the bias and precision. Finally, it should be noted that during both 1984 and 1985, the analytical bias and precision measurements for all analytes measured at the CAL were within the acceptable limits specified in the Quality Assurance Plan (2).

B. REPLICATE SAMPLE DATA

From the inception of the program, replicate samples were analyzed and the data used to evaluate laboratory precision. These splits were made in the sample processing section of the lab. Three filtered 60 mL aliquots were collected from 4% percent of the precipitation samples arriving at the CAL. The same laboratory sample number was given to each of the samples, with the first aliquot taken being designated A and the second, B. The third aliquot was refrigerated for storage in the sample archives. Samples A and B were subsequently placed side by side on a sample tray and submitted for analysis. Typically, the analysis of the B sample immediately followed analysis of the A sample. The fact that these were two aliquots of the same sample was known to all of the analysts.

In July 1984 a change was made in the replicate procedures. Four percent of the samples received by the CAL continued to be split into three 60 mL portions. Half of these splits were treated as described above and labeled with an NADP/NTN sample number followed by an A or a B. The other half were labeled and analyzed very differently. The first and third aliquots were labeled with the NADP/NTN sample number. The first aliquot was placed on the sample tray and sent to the laboratory for analysis. The third aliquot was put into refrigerated storage. The second aliquot was returned to the receiving area where it was given a new sample number. This step could require one or two days, after which the sample would be placed on the tray being sent for analyses. Careful records were maintained by the Quality Assurance Specialist and the data processing staff to assure that the original sample number and the new sample number were available for later use in interpreting the results of these replicate analyses; however, these samples remained blind to the analysts. After all analyses had been performed, but before the data were entered into the computer, the sample number was changed on the second aliquot to the original sample number followed by a Q. These blind splits will subsequently be referred to as O/Q pairs.

This section of the report discusses the plots of the data derived from both the A/B and the O/Q replicate analyses. The plots are presented as Figures 1 through 40 in Appendix C. They are arranged by parameter, with each figure representing one year's analyses. They are also grouped by split type with all of the A/B data presented first, and followed by those for the O/Q pairs. Interpretation of the data and a summary statement about laboratory precision for 1984 and 1985 are included.

1. Range Selection

The figures in Appendix C are plots of the concentration differences between replicate samples A and B (or O and Q) in mg/L versus the average concentrations of A and B (or O and Q) in mg/L. The differences are always calculated by using the formula [analyte concentration of A (O) minus analyte concentration of B (Q)]. The average is [analyte concentration of A (O) plus analyte concentration of B (Q)] divided by 2. To facilitate the usefulness of the plots, the yearly assessments for each ion have been split into two sections. A median concentration for the two-year period was determined for each analyte. The first plot in each figure includes the range from 0 mg/L to the median concentration of the analyte of interest. The second plots of the figures begin with the 50th percentile concentration value and continue to the 95th percentile concentration of that analyte found in the replicate samples analyzed during the period. Table IV-6 lists the 50th percentile and the 95th percentile concentrations for each analyte for the replicate samples analyzed in 1984 and 1985.

TABLE IV-6 Fiftieth and Ninety-fifth Percentile Concentration Values of Chemical and Physical Parameters Measured in Precipitation Samples Selected for Replicate Analyses in 1984-1985.

Parameter	**Percentile Concentration Values (mg/L)** **50th**	 **95th**
Calcium	0.100	1.00
Magnesium	0.035	0.225
Sodium	0.075	0.750
Potassium	0.025	0.125
Ammonium	0.15	1.50
Sulfate	1.20	6.00
Nitrate	1.00	5.00
Chloride	0.15	3.00
pH (units)	4.50	3.64
Specific Conductance (uS/cm)	15.0	75.0

2. Tables and Plots

Figures 1 through 40 in Appendix C are plots of the differences found at the CAL between two aliquots (A/B) of the same precipitation sample analyzed in succession, and two aliquots (O/Q) of the same precipitation sample analyzed at different times. The plots are grouped by analyte, and each figure contains both low and high concentration plots for a single year. Plots of the difference between A and B (or O and Q) are presented for all analytes except orthophosphate. The number of precipitation samples containing orthophosphate is small, and the number of replicate samples containing differences greater than 0.000 mg/L in the orthophosphate concentrations is even smaller. For the A/B replicate pairs, 88.3% of the samples analyzed in 1984 and 85.4% of those analyzed in 1985 contained no measureable orthophosphate. Of the 11.7% of the samples analyzed in 1984 and the 14.6% analyzed in 1985 containing orthophosphate, the difference between the orthophosphate concentration measured in samples A and B was 0.000 mg/L for all but 2% of the samples. For the O/Q replicate pairs, 77.8% of the samples analyzed in 1984 and 77.3% of those analyzed in 1985, contained no measureable orthophosphate. Of the 22.% (1984) and 22.7% (1985) of the O/Q pairs that contained the analyte, all had differences of 0.000 mg/L. Plots of these differences were deemed unnecessary.

Table IV-7 lists the mean differences for each analyte for both A/B and O/Q sample pairs for the two years. Tables 1 through 4 in Appendix C present complete annual statistical summaries of the differences plotted in Figures 1 through 40.

TABLE IV-7 Mean Differences for Replicate Analyses of Precipitation Samples for 1984-1985.

	Mean Difference (mg/L)			
	1984		1985	
Parameter	(A/B)[a]	(O/Q)[b]	(A/B)[a]	(O/Q)[b]
Calcium	0.001	-0.003	0.000	-0.001
Magnesium	0.000	-0.001	0.000	0.000
Sodium	0.000	0.007	0.000	0.000
Potassium	0.000	-0.006	-0.001	0.000
Ammonium	0.00	0.00	0.00	0.00
Sulfate	0.01	0.01	-0.01	-0.01
Nitrate-Nitrite	0.00	0.01	-0.01	-0.01
Chloride	0.00	0.01	0.00	0.01
pH (units)	0.00	-0.01	0.00	-0.01
Specific Conductance (uS/cm)	-0.1	-0.2	0.0	-0.1
n[c]	231	108	177	176

a. (A/B) = aliquots of same precipitation sample analyzed in succession
b. (O/Q) = aliquots of same precipitation sample analyzed at different times
c. number of replicate pairs

3. Discussion of Results

The data presented in both the figures and the tables indicate that the precision at the CAL for splits analyzed in succession was always very good. The differences are almost always within three times the MDL for each analyte and in most cases are within two times the MDL. Precision of this quality is what should be expected for these types of analyses where the analyses are performed in succession.

The O/Q pairs show larger differences between the two analyses or less precision in the measurements. This is what would be predicted of sample pairs analyzed as blinds and at different times. The time period between the analyses of the two samples may be sufficient for changes in the ionic composition of the sample to occur. Despite this possibility, a comparison of the differences found in both the A/B and the O/Q pairs for 1984 and 1985 indicates that the precision for these samples is satisfactory for all analytes.

C. INTERNAL BLIND SAMPLE DATA

In July 1984 an internal blind sample program was started to provide still another means of assessing the quality of the CAL data. Samples of known analyte concentrations were prepared by the Quality Assurance Specialist and submitted to the sample processing staff at a frequency of two samples per week. In the processing laboratory, the samples received an NADP/NTN sample identification number, and an aliquot of each was removed for later measurement of pH and specific conductance. The samples were filtered, placed on a sample tray, and sent to the analytical staff for routine analysis.

Although the sample processing staff were aware of the fact that these were not precipitation samples, they did not know the expected analyte concentrations of the samples. The remaining CAL analytical staff were not only unaware of the analyte concentrations of these samples, but were also unaware which samples on the trays were synthetic.

The following sections of this report provide more detail on the samples that were used in the internal blind program. Tables of the analytical bias and precision calculated from the data resulting from the analysis of these samples, as well as a discussion of what the data in these tables indicate about the performance of the CAL, are included.

1. Solutions Used

Samples of known analyte concentrations were obtained from the U.S. Environmental Protection Agency in Research Triangle Park, North Carolina. These samples were originally prepared for a USEPA/WMO laboratory intercomparison that took place in October 1983. The samples contain all of the routine parameters, except for orthophosphate, that are determined in the network samples. The analyte concentration levels are comparable to those found in the network samples. Both of these factors made these samples preferable to samples that were dilutions of the EPA drinking water reference samples used as QCS.

Three different samples, with directions for dilution and a table of analyte concentrations that should result from the dilution, were supplied to the CAL. These samples had been checked by the USEPA for both accuracy and stability. The stability was also monitored by the CAL QA Specialist, and new dilutions were made whenever warranted. Only one liter of each sample was prepared because of the presence of unstable species such as nitrate and the possible need for frequent preparations of the samples to maintain these analytes at the expected levels.

In 1984, all three samples were diluted as directed by the USEPA and used in the program. Two of these samples, however, contained higher concentrations of most analytes than were normally found in the network. By diluting these two samples further, by a factor of 10, the resultant analyte levels were very similar to those in the network samples. These additionally diluted samples were used for the program throughout 1985. This second dilution increased the instability of both the nitrate and the ammonium ions and required more frequent sample preparation.

2. Analytical Bias and Precision Tables

The data that resulted from the analyses of these samples are contained in Tables IV-8 and IV-9. These tables contain similar information to that found in Tables IV-4 and IV-5 for replicate analyses of QCS. There is a difference, however, in the procedure used to determine whether the calculated bias was or was not significant.

The calculation for the critical percent used to determine the significance of the calculated bias is given in the Glossary (Appendix A). That formula was used with the QCS data because the standard deviation of the true value and the number of analyses used to determine the value and the standard deviation were supplied by the USEPA. This information was not available for the USEPA/WMO samples used in the internal blind program. Instead, a confidence interval was calculated for the laboratory mean using the following formula recommended by Taylor (7):

$$\text{Confidence Interval} = \bar{x} \pm (t_{.95}s)/\sqrt{n}$$

where $\bar{x}$ = laboratory sample mean

$t_{.95}$ = the t value at the 95% confidence interval for n-1 degrees of freedom

s = sample standard deviation

n = number of analyses

When the recommended or true value lies within this confidence interval, the bias is not considered significant. When that value is outside of the interval, it is said to be significant. This is how the significance of the bias was determined for the bias calculated from the analyses of the internal blind samples. The results appear in the last columns of Tables IV-8 and IV-9.

3. Discussion of Results

Comparison of the bias and precision calculated from replicate analysis of QCS (Tables IV-4 and IV-5) to those obtained from analysis of the internal blinds (Tables IV-8 and IV-9) indicate that bias and precision are better for known samples than for unknowns. What is

TABLE IV-8 1984 Analytical Bias and Precision from Internal Blind Audit Program.

Parameter	Recommended Concentration (mg/L)	Number Samples (n)	Mean Concentration Measured (mg/L)	Bias[a] (mg/L)	Precision[b] (% RSD)	Bias[c] Significant ?
Ca^{+2}	0.110	19	0.111	0.001	6.2	No
	2.060	15	1.858	-0.202	1.9	Yes
	3.630	18	3.203	-0.427	1.9	Yes
Mg^{+2}	0.010	19	0.009	-0.001	17.3	Yes
	0.250	15	0.249	-0.001	2.4	No
	0.370	18	0.369	-0.001	1.9	No
K^{+}	0.050	19	0.054	0.004	4.5	Yes
	1.470	18	1.493	0.023	2.5	Yes
	2.680	15	2.684	0.004	1.8	No
Na^{+}	0.080	19	0.084	0.004	5.2	Yes
	0.260	15	0.261	0.001	2.4	No
	1.440	18	1.461	0.021	2.2	Yes
SO_4^{-2}	1.71	19	1.62	-0.09	4.3	Yes
	11.14	18	10.65	-0.49	5.2	Yes
	17.73	15	16.18	-1.55	9.8	Yes
NO_3^{-}	0.13	19	0.14	0.01	16.2	No
	4.52	15	4.25	-0.27	1.6	Yes
	6.11	18	5.84	-0.27	7.8	Yes
Cl^{-}	1.01	19	1.04	0.03	2.1	Yes
	4.17	15	4.21	0.04	2.2	No
	10.33	18	10.00	-0.33	4.8	Yes
NH_4^{+}	0.42	19	0.40	-0.02	10.4	No
	0.44	15	0.43	-0.01	3.4	Yes
	2.31	18	2.23	-0.08	3.9	Yes
pH (units)	3.49	15	3.50	0.01	5.6	No
	3.72	18	3.73	0.01	6.8	No
	4.45	19	4.48	0.03	8.5	Yes
Conductivity (uS/cm)	19.0	19	19.7	0.7	2.3	Yes
	135.0	18	135.6	0.6	1.7	No
	165.8	15	164.6	-1.2	1.8	No

a. Bias = (Measured Concentration - Recommended Concentration)

b. % RSD = (Standard Deviation/Mean Measured Concentration) X 100; precision of pH measurements expressed in terms of hydrogen ion concentration

c. Calculated from 95% confidence interval of measured mean concentration. If this interval includes the recommended concentration, reported bias is not significant.

TABLE IV-9 1985 Analytical Bias and Precision from Internal Blind Audit Program

Parameter	Recommended Concentration (mg/L)	Number Samples (n)	Mean Concentration Measured (mg/L)	Bias[a] (mg/L)	Precision[b] (% RSD)	Bias[c] Significant ?
Ca^{+2}	0.206	45	0.197	-0.009	4.4	Yes
	0.363	46	0.327	-0.036	2.9	Yes
Mg^{+2}	0.025	45	0.033	0.008	14.5	Yes
	0.037	46	0.043	0.006	8.8	Yes
K^{+}	0.147	46	0.150	0.003	4.2	Yes
	0.268	45	0.274	0.006	2.8	Yes
Na^{+}	0.026	45	0.047	0.021	28.2	Yes
	0.145	46	0.166	0.021	8.9	Yes
SO_4^{-2}	1.11	46	1.07	-0.04	6.3	Yes
	1.77	45	1.70	-0.07	7.8	Yes
NO_3^{-}	0.45	45	0.37	-0.08	41.2	Yes
	0.61	46	0.62	0.01	9.2	No
Cl^{-}	0.42	45	0.45	0.03	5.5	Yes
	1.03	46	1.04	0.01	11.6	No
NH_4^{+}	0.04	45	0.01	-0.03	75.4	Yes
	0.23	46	0.14	-0.09	65.0	Yes
pH (units)	4.48	45	4.49	0.01	7.6	Yes
	4.73	46	4.71	-0.02	7.2	Yes
Conductivity (uS/cm)	13.7	46	14.7	1.0	3.1	Yes
	16.6	45	18.1	1.5	3.2	Yes

a. Bias = (Measured Concentration - Recommended Concentration)

b. % RSD = (Standard Deviation/Mean Measured Concentration) X 100; precision of pH measurements expressed in terms of hydrogen ion concentration

c. Calculated from 95% confidence interval of measured mean concentration. If this interval includes the recommended concentration, reported bias is not significant.

important to note is that while the blind sample data appear somewhat more biased and less precise, the accuracy is within the limits set in the QA Plan (2).

There are several additional points that should be raised about the data contained in Tables IV-8 and IV-9. First, the sodium for both years is biased high and those biases were generally considered significant. The QCS data show that the problem does not lie with the analytical method. The problem is believed to result from the handling procedures for the blind samples. These included the use of two or more sample containers and filtration. Such additional handling always increases the potential of sample contamination, with sodium being the most likely contaminant.

The possible disappearance of the unstable nitrate and ammonium ions has already been suggested in the discussion of QCS and replicate analysis results. Although all of the raw data for these unstable ions have not been supplied for review, they show steadily decreasing concentrations of the ions with each sample taken. Predictably, preparation of a new sample dilution results in nitrate and ammonium values at theoretical levels. This fact is most apparent in the precision for the two analytes. In an attempt to eliminate the problem, samples were prepared monthly. Even with this procedure, decomposition occurred at varying rates and the data obtained from the analysis of these samples are not a reliable indicator of laboratory bias or precision.

Finally, as with the QCS data, most of the data from the blind sample program show a statistically significant bias. Examination of the amount of the bias in milligrams per liter shows that the actual deviations from the true values are often extremely small and of no real concern to the data user. Because the samples analyzed as part of this program receive very similar handling to the network samples, the estimates of bias and precision derived for the stable ions in these samples provide better approximations of the accuracy of the network sample measurements than the data obtained from the analysis of the known QCS solutions.

V. REANALYSIS PROCEDURES

Once the analyte concentrations in a precipitation sample are determined, the information is entered into the CAL data base. The analyte concentrations are converted from milligrams per liter to microequivalents per liter, and an ion balance calculation is made for each sample. The information resulting from this calculation is used to select approximately 8% of the samples for reanalysis.

A detailed explanation of different ion balance calculations appeared in the Laboratory Quality Assurance Report for 1978-1983 (1) and will not be repeated here. It is important to know which method a laboratory employs, however, not only for purposes of data comparisons, but also for data interpretation, particularly when this information will be used to evaluate laboratory performance.

The calculation method used by the CAL is described in Figure V-1. The factors used to convert the measured analyte concentrations from milligrams per liter to microequivalents per liter are listed in Table V-1. These were taken from Standard Methods for the Examination of Water and Wastewater (8).

Ion balance calculations are a valuable component of the CAL quality assurance program. A large imbalance can be indicative of an error in the analyses. It may also be an indication that additional ionic species are present in the sample and further analyses are

NADP/NTN Ion Balance
Calculation Method

$$\text{Ion \% Difference} = \frac{(\text{Anions} - \text{Cations})}{(\text{Anions} + \text{Cations})} \times 100$$

$$\text{Anion}^{*} = (SO_4^{-2}) + (NO_3^{-}) + (Cl^{-}) + (PO_4^{-3}) + (OH^{-}) + (HCO_3^{-})$$

$$\text{Cation}^{*} = (Ca^{+2}) + (Mg^{+2}) + (Na^{+}) + (K^{+}) + (NH_4^{+}) + (H^{+})$$

* Concentrations are expressed in microequivalents/liter

FIGURE V-1. Formula used by the CAL to calculate an ion percent difference (IPD)

TABLE V-1 The Factors Used to Convert Analyte Concentrations from Milligrams per Liter to Microequivalents per Liter.[a]

Analyte	ueq/L = mg/L x
Calcium	49.90
Magnesium	82.26
Sodium	43.50
Potassium	25.57
Ammonium	55.44
Sulfate	20.83
Nitrate	16.13
Chloride	28.21
Orthophosphate	31.59

a. Factors taken from Standard Methods for the Examination of Water and Wastewater (8).

necessary to completely characterize the sample. By selecting a maximum allowable imbalance and reanalyzing all samples with an imbalance greater than this maximum, an imbalance that resulted from analytical error can be found and corrected.

In the following sections, the criteria used to select samples for reanalysis are presented. Discussions of the information that can be derived from these reanalysis procedures and how this information is used to change the original analytical data are also included.

A. ION BALANCE CRITERIA

In October 1981, a set of criteria was developed to select samples for reanalysis due to a large ion imbalance. These criteria were selected after an examinaton of the data from the previous three years of network operation. Regional differences in rainfall amounts and analyte concentrations were compared, and the criteria that had been used since 1979 (1) were altered to better select those samples which were truly outliers. The goal was to select 5-6% of the samples analyzed at the CAL for reanalysis. Time has proven this to be an adequate set of criteria to reach the desired goal, and it has remained unchanged since its formulation in 1981.

The computer program that calculates an ion balance for each sample also determines the ion sum (IS) or total ionic strength of the sample. The analyte concentrations have already been converted to microequivalents per liter as part of the ion balance calculation. To obtain the ion sum (IS), the total anion concentration expressed in microequivalents is added to the total cation concentration, also in microequivalents. Both the ion sum and the ion percent difference that result from the ion balance calculation are used to determine which samples should be reanalyzed. The ion balance criteria for reanalysis selection are:

When IS $<$ 50 ueq/L, reanalyze if IPD $> \pm$ 60%;

when 50 $\leq$ IS $<$ 100 ueq/L, reanalyze if IPD $> \pm$ 30%; and

when IS $\geq$ 100 ueq/L, reanalyze if IPD $> \pm$ 15%

where IS = Ion Sum = (Anion + Cation) ueq/L, and

$$\text{IPD} = \text{Ion Percent Difference} = \frac{(\text{Anion} - \text{Cation})}{(\text{Anion} + \text{Cation})} \times 100$$

B. SPECIFIC CONDUCTANCE CRITERIA

Another part of the ion balance program uses the measured concentration of analytes to calculate a theoretical conductance for the sample. The formula used is:

$$\begin{aligned}\text{Calculated Conductance} = [&(H^{+})(350) + (HCO_3^{-})(43.6) + \\ &(Ca^{+2})(52.0) + (Cl^{-})(75.9) + (Mg^{+2})(46.6) + \\ &(K^{+})(72.0) + (Na^{+})(48.9) + (NO_3^{-})(71.0) + \\ &(SO_4^{-2})(73.9) + (NH_4^{+})(72.5)] \div 1000\end{aligned}$$

where ion concentrations are expressed as microequivalents per liter.

The conductance factors used in this calculation for hydrogen ion and ammonium can be obtained from the CRC Handbook of Chemistry and Physics (9). The remaining factors can be found in Standard Methods for the Examination of Water and Wastewater (8).

The calculated conductance is compared to the measured conductance, and a conductance percent difference is found. This comparison uses the following equation:

Conductance Percent Difference = CPD =

$$\frac{(\text{Calculated Conductance} - \text{Measured Conductance})}{\text{Measured Conductance}} \times 100$$

Once the CPD has been calculated, it can be used as another means of selecting samples for reanalysis. It was not until 1981 that suitable criteria were developed to utilize this CPD information. As with the ion percent difference, a large CPD may indicate a measurement error in one or more of the analytes. Percentile values for measured specific conductance from 1978-1981 were used to formulate a set of CPD criteria that were added to the ion balance program in October 1981. The CPD criteria are:

When measured conductance $\leq$ 10 uS/cm,
reanalyze if CPD > ± 65%;

when 10 uS/cm < measured conductance $\leq$ 30 uS/cm,
reanalyze if CPD > ± 45%;

when 30 uS/cm < measured conductance $\leq$ 50 uS/cm,
reanalyze if CPD > ± 30%; and

when measured conductance > 50 uS/cm,
reanalyze if CPD > ± 20%.

The percentage of samples that meet these criteria is generally less than 2%, and most often they have already been flagged because of an ion imbalance. Nevertheless, this provides another means of detecting large analytical errors and is a useful calculation to perform.

C. HISTOGRAMS

Figures V-2 through V-5 are histograms of the ion percent difference values (IPD) and the conductance percent difference values (CPD) for the samples from the NADP/NTN network for the years 1984 and 1985. With each histogram, a median, a mean, and a standard deviation are noted.

The IPD histograms approximate a normally distributed curve centering around the 0% difference point. This is what one would expect if the sample analysis includes the measurement of all of the major anions and cations in precipitation. The eleven parameters selected for analysis at the CAL appear to adequately characterize the precipitation samples collected within the NADP/NTN network. Again, a normal distribution around the 0% difference point would be expected for the CPD histograms. However, it does not occur. These plots have a negative skew. The calculated conductance is typically less than the measured conductance. This suggests either a measurement or a calculation problem. Specific conductance values obtained for quality control samples with certified conductivity values are consistently within the acceptable limits. This suggests that the accuracy of the specific conductance measurements is good. A problem in the calculations was investigated as one source of the skewed curve. Using the constants found in the CRC Handbook (9) instead of those in Standard Methods (8) to determine the calculated specific conductance results in a population mean difference closer to 0%. The change to these constants was put into effect beginning in March 1987. This negative skew may also be the result of the presence of ions not being routinely measured by the CAL. The curve is centering near -10% in most years, which may result from the presence of low concentrations of ions whose presence goes undetected in the IPD calculations and resultant histograms. The presence of trace amounts of metal ions complexed with unmeasured

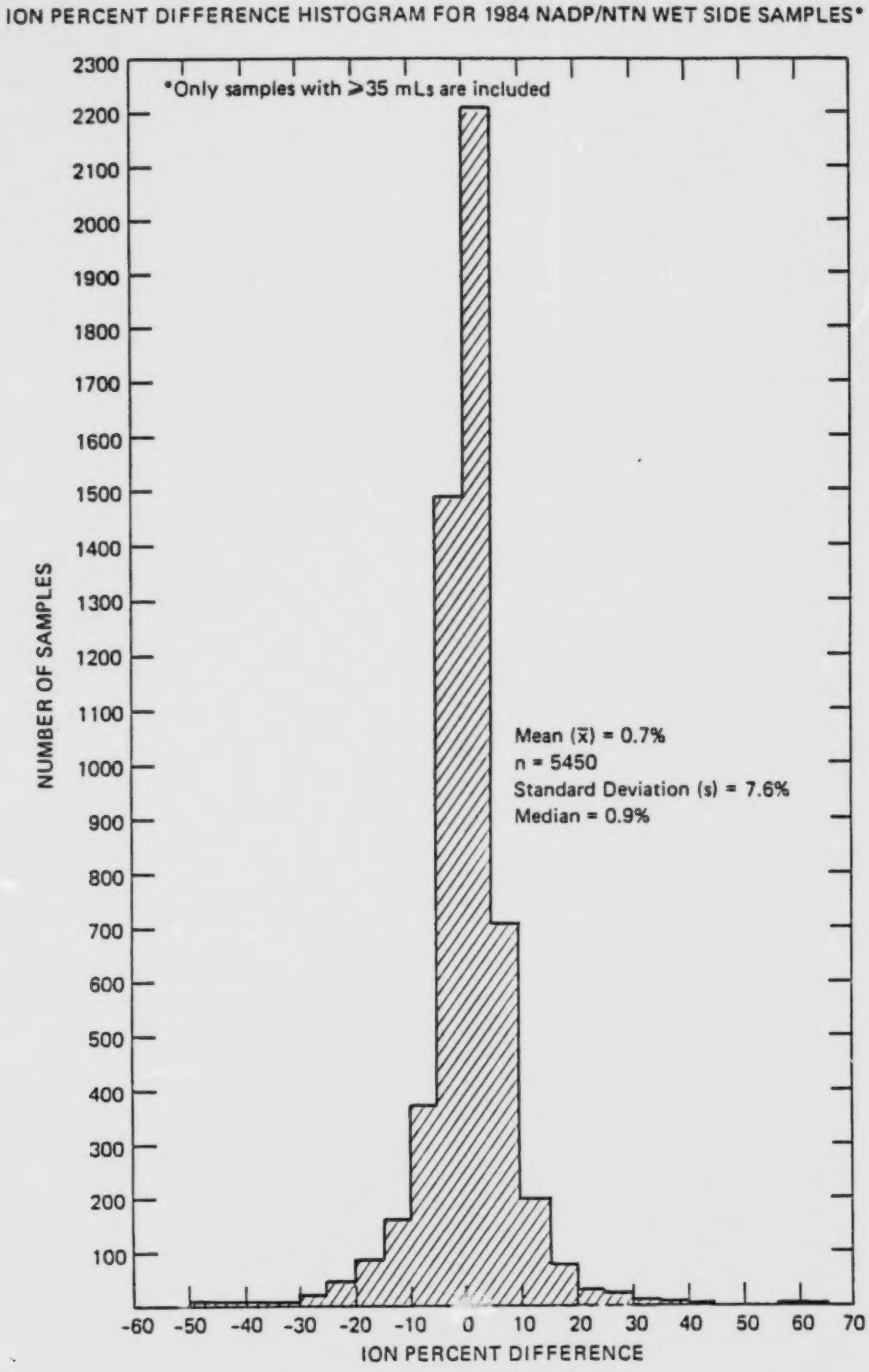

FIGURE V-2. Ion percent difference histogram for NADP/NTN wet side samples in 1984.

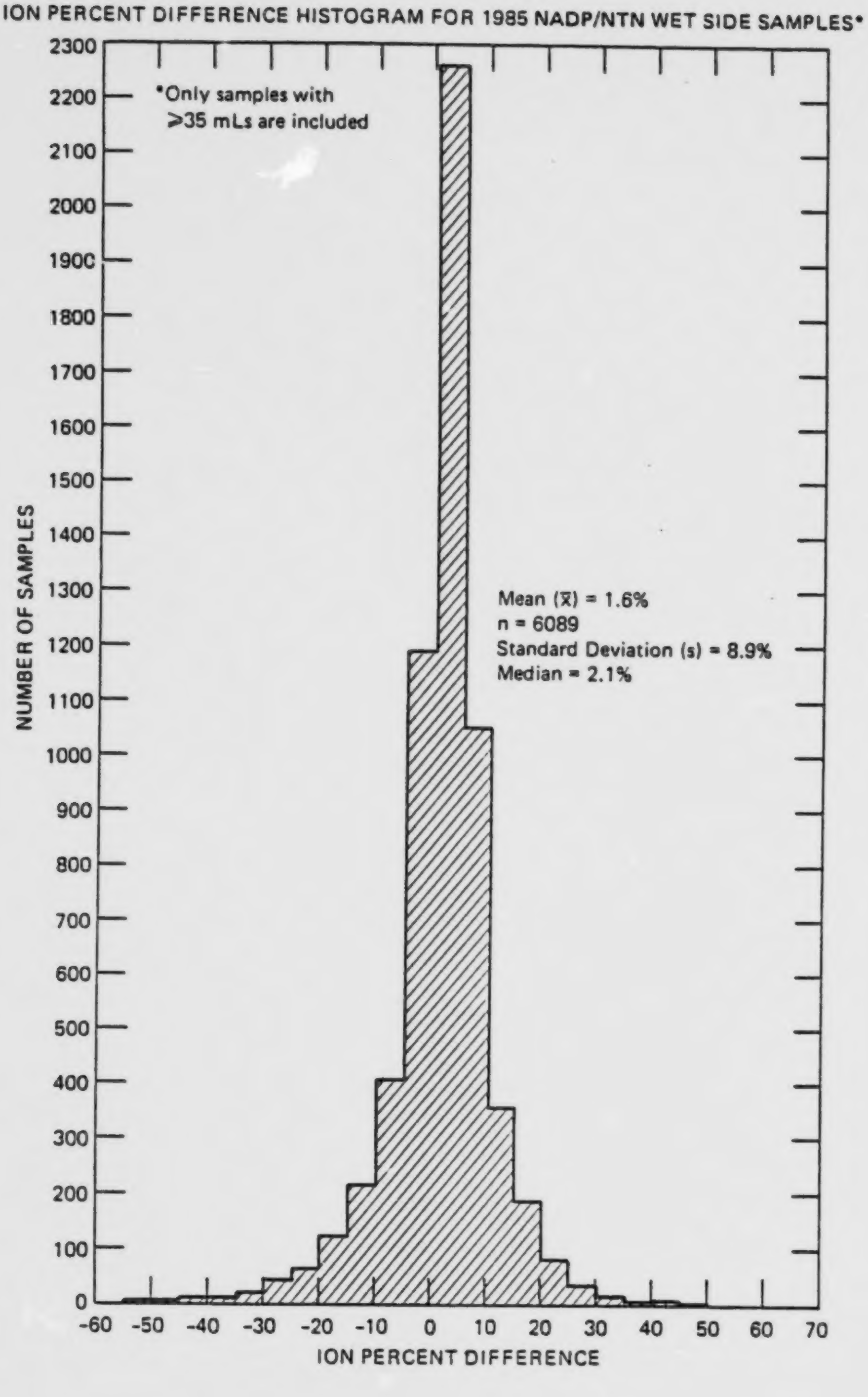

FIGURE V-3. Ion percent difference histogram for NADP/NTN wet side samples in 1985.

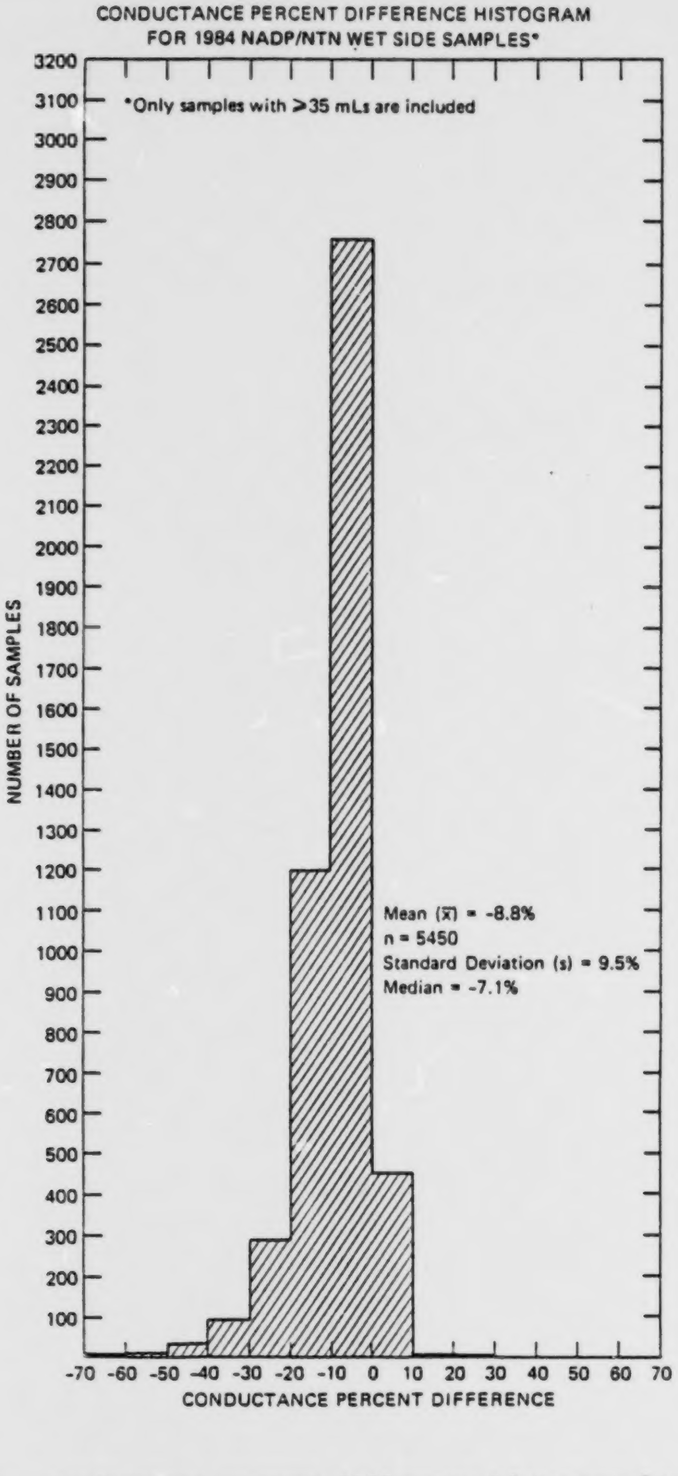

FIGURE V-4. Conductance percent difference histogram for NADP/NTN wet side samples in 1984.

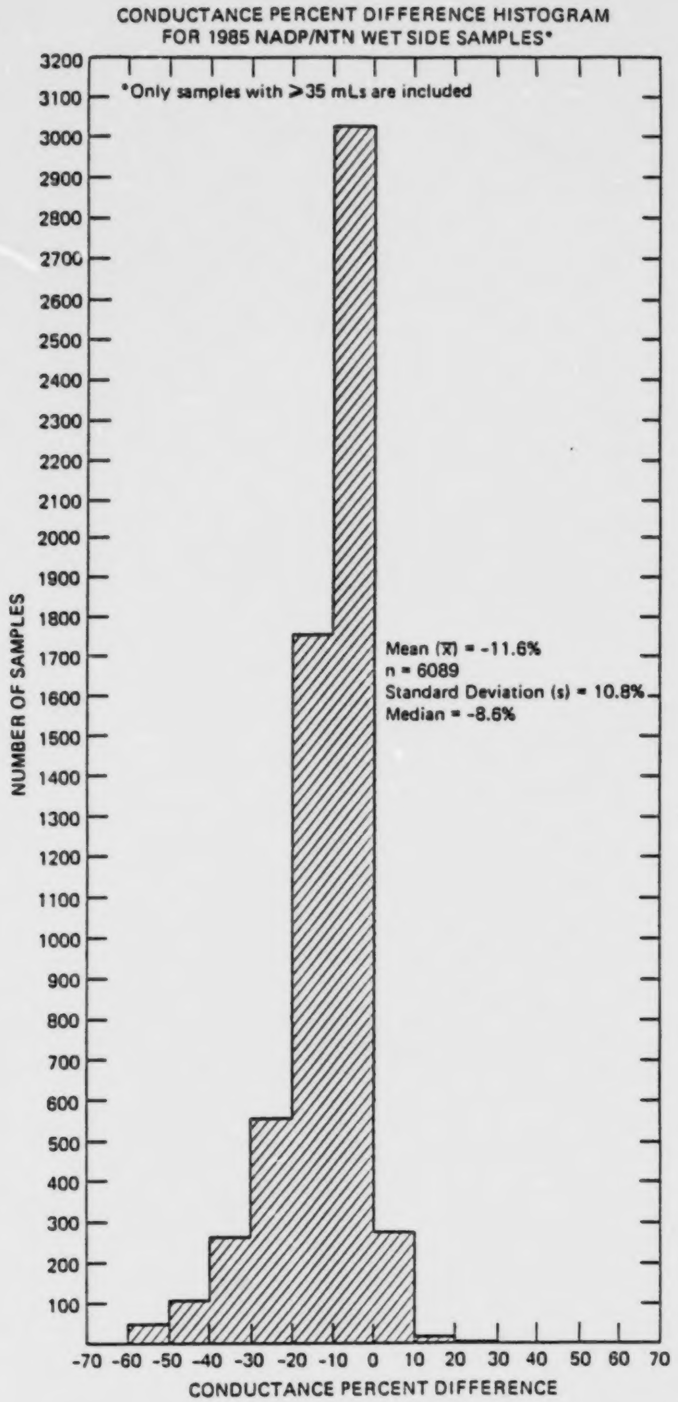

FIGURE V-5. Conductance percent difference histogram for NADP/NTN wet side samples in 1985.

anions, such as bromide, could go undetected by the ion balance calculation but result in a negative conductance percent difference.

D. DISCUSSION OF RESULTS

The fact that a sample does not satisfy the criteria previously described and is selected by the program for reanalysis does not necessarily mean it will be reanalyzed. Reanalysis may be impossible simply because all of the sample was used during the initial analyses. Also, A/B and O/Q splits are not reanalyzed if the original duplicate analyses were the same or very similar to each other. All other samples flagged by the ion balance program are retrieved and reanalyzed for all constituents.

Once the reanalysis has been completed, the new data are compared to the original data. When substantial differences are found between the two results, reasons for the difference are sought. The first step is to analyze the refrigerated aliquot when one is available. Since refrigeration is a means of sample preservation, the integrity of the refrigerated aliquot should have been maintained. If the difference was the result of decomposition of the sample stored at room temperature, this will be apparent. When the results from the analysis of the refrigerated aliquot are more like the reanalysis value, the source of the error in the original analysis is sought. Analysts' input as to the possible source of error is always utilized to explain discrepancies between original and reanalysis results.

When a difference in original and reanalysis values occurs and no explanation can be found, the original data are reported. If the difference is explained, the data will be changed and a new value reported. For all of the samples reanalyzed, less than 1% will require any change in the original data. The overall result is that approximately 0.1% of the final data is changed from the value that was initially reported.

VI. EXTERNAL QUALITY ASSURANCE PROGRAM PARTICIPATION

The analytical bias and precision data reported in Section IV are supported by the CAL's performance in several different external quality assurance programs. One program, operated by the U.S. Geological Survey (USGS), audits the CAL's performance for the NADP/NTN program. In addition to this external quality assurance program, the CAL voluntarily participates in other national and international performance studies. The performance of the CAL in each of these studies is addressed below.

A. U.S. GEOLOGICAL SURVEY EXTERNAL AUDIT PROGRAM

The U.S. Geological Survey's external audit program for the CAL has two components: a blind sample program and an interlaboratory comparison study. The data obtained from these programs provide information about not only the CAL's performance but also the effects of sample handling in the field.

The NADP/NTN Blind Audit Program that started in October 1979 (10) continued with only minor changes through 1985. During the years 1984 and 1985, the USGS reformulated some of the Standard Reference Water Samples (SRWS) being supplied to sites in the sampling network so the resultant analyte concentrations in these SRWS more closely resembled those found in network precipitation samples. During 1984 and 1985, Nanopure deionized water from the USGS National Water Quality Laboratory in Denver, Colorado, the dilute nitric acid quality control check solution prepared by the CAL, and National Bureau of Standard certified simulated rainwater samples were made available for possible use in the program.

The first week a site did not have rain, the site operator was directed to pour the sample he/she had previously received from the USGS into a clean bucket and submit it to the CAL as the rain sample for the week. The site operator was to notify the USGS and the Coordinator's Office of the date that the blind sample had been sent. The sample would subsequently be processed by the CAL as a routine precipitation sample. This program relies heavily on the cooperation of the site operators. The data from the analyses of these external blind samples reflect the effects of the sample handling from the time it is bottled at the USGS until it is analyzed at the CAL.

The audit program focuses on the analytical data obtained from the analysis of the samples for calcium, magnesium, sodium, potassium, sulfate, and chloride. Despite the reformulations of the sample composition by the USGS mentioned earlier, many of the SRWS used in the program through 1985 had analyte concentrations higher than those found in rainwater and often required dilution by the laboratory before analysis. Table VI-1 lists the maximum analyte concentration that can be present in a sample before a dilution is necessary. The fact that a dilution of the sample has been made adds another variable to be considered when interpreting the data. The USGS has issued three reports that analyze the data from the blind audit program from January 1980 through December 1985 (11, 12, 13). Inquiries about additional details of this program should be directed to the USGS, Denver Federal Center, Denver, Colorado.

TABLE VI-1 Maximum Analyte Concentration Measured Before Sample Dilution Is Required.

Analyte	Concentration (mg/L)	Dates
Calcium	3.00	1/79 - 12/83
Magnesium	1.00	1/79 - 12/83
Sodium	1.00	1/79 - 12/83
Potassium	1.00	1/79 - 12/83
Ammonium	2.00	1/79 - 12/83
Sulfate	10.00 9.00	1/79 - 1/83 1/83 - 12/83
Nitrate-Nitrite	5.00	1/79 - 12/83
Chloride	5.00 3.00	1/79 - 4/81 4/81 - 12/83
Orthophosphate	0.100 0.250	1/79 - 1/83 1/83 - 12/83

The USGS interlaboratory comparisons were started in the late fall of 1982. Participants in the study were: Inland Waters Directorate, Ontario, Canada (IWD); Illinois State Water Survey, Champaign, Illinois (CAL); U.S. Geological Survey National Water Quality Laboratory, Atlanta, Georgia (ATL); and U.S. Geological Survey National Water Quality Laboratory, Denver, Colorado (DEN). In 1984, the Bituminous Coal Research Laboratory (BCR) was briefly added as a participant in the program. In November 1985, the USGS laboratories in Atlanta and Denver were consolidated; therefore, the USGS report for the 1985 intercomparison (13) includes data for only the first nine months of 1985 for all of the participating laboratories.

This intercomparison study was designed to determine whether the four participating laboratories were producing comparable results. At each laboratory, analytical bias was documented, and estimates of analytical precision were made. Precipitation samples from sites in the NADP/NTN network were split at the CAL and sent to the USGS National Water Quality Laboratory in Denver. The samples were renumbered at the USGS and distributed to each of the four participants for analysis. In addition to natural precipitation samples, synthetic samples of known analyte concentrations were also routinely submitted to the participating laboratories for analysis. Data obtained from the analysis of calcium, magnesium, sodium, potassium, ammonium, sulfate, nitrate, chloride, pH, and specific conductance were subsequently returned to the Denver facility. Water-Resources Investigations Reports 87-4067 (14) and 87-4219 (13) discuss the USGS analysis of the data received from October 1983 - December 1985.

B. INTERLABORATORY COMPARISON STUDIES

During 1984 and 1985, the CAL participated in several other interlaboratory performance studies in addition to the USGS-sponsored comparisons just discussed. These studies were sponsored by state and federal government agencies as well as international organizations. This section continues with a brief description of the studies in which the CAL participated. The CAL data for each study under discussion are presented in Tables 1 through 10 in Appendix D. These tables also include the expected or target concentrations of each analyte. Summary information on the CAL's performance in these studies is included in this section. More detailed explanations of the laboratory intercomparisons are contained in the agency summaries in the reference list at the end of this report.

1. World Meteorological Organization/ United States Environmental Protection Agency (WMO)

In an attempt to establish cooperation among international precipitation laboratories and to better evaluate its network data, the World Meteorological Organization (WMO) selected a Precipitation Reference Laboratory (PRL) in 1975. It designated the Environmental Monitoring Systems Laboratory (EMSL) of the U.S. Environmental Protection Agency, Research Triangle Park, N.C., to be this PRL and directed it to achieve the goals it had set by designing and conducting interlaboratory comparison studies (15).

Details of the CAL's participation in the WMO intercomparison program from 1980-1983 were presented in the laboratory Quality Assurance Report for 1978-1983 (1). The CAL's participation in this program continued in 1984 and 1985. During this period there were four intercomparison studies. Tables 1 through 4 in Appendix D compare the CAL data to the expected analyte concentrations for these four intercomparison studies. The data in these tables indicate continued good performances by the CAL.

Table VI-2 summarizes the CAL performance for all WMO studies in which the laboratory had participated by the end of 1985. This table provides the mean percent deviation of the CAL reported values from the WMO expected values for the 10 principal constituents routinely analyzed in precipitation. Analysis for orthophosphate is not included in these intercomparison studies. Table VI-2 also includes the mean percent deviation values from the WMO expected values for all participating laboratories. The data presented in this table combine those which first appeared in the ISWS 20th (16) and 21st (17) Progress Reports to the U.S. Department of Energy.

In each of the WMO interlaboratory comparisons, the CAL also determined acidity and trace metal concentrations for the test samples. Information regarding these analyses can be found in the final reports for each study. Most of the participants in these studies do not routinely include trace metals in their analytical results. Trace metal analyses are also not performed for the network samples. For these reasons, only the 10 major chemical and physical parameters routinely

TABLE VI-2 Summary of Results from World Meteorological Organization (WMO) Interlaboratory Comparison of Reference Precipitation Samples.[a]

Intercomparison Number	Date	Number of Participating Laboratories (n)	Mean % Difference[b] From Expected Value CAL	Mean % Difference[b] From Expected Value All Labs
Four	7/80	27	4.38	17.67
Six	4/83	22	3.89	17.47
Seven	11/83	22	2.65	23.51
Eight	4/84	22	4.73	39.53
Nine	10/84	25	6.49	43.82
Ten	4/85	27	3.61	33.04
Eleven	10/85	23	3.57	19.19

a. Chemical parameters used in the calculation were Ca, Mg, Na, K, NH_4,NO_3, Cl, SO_4, pH, and Specific Conductance.

b. Mean % Difference = $$\frac{\frac{|\text{Expected Value} - \text{Reported Value}|}{\text{Expected Value}}}{10\ (\text{constituents})} \times 100$$

measured by the CAL and a large number of participating laboratories are included in this summary table. The data presented for each summary represent pooled results for the analysis of the measured constituents in three samples (17). The percent deviations were calculated for the combined laboratory data set after outliers were removed. The method used to classify which results were outliers is detailed in the WMO study summary (15). Each participating laboratory received a listing of the true values for the samples analyzed as part of the study and a percentile listing of the percent deviations from the true values for each parameter, both for all analyses and for those that remained once the outliers were removed. Mean percent deviations for each parameter, both with and without outliers, were also included in these study summaries. The CAL did not receive published study reports for the studies conducted in 1984 and 1985; however, information about these studies can be obtained from the PRL.

An examination of the data in Table VI-2 indicates that the CAL continued to produce high-quality analytical data during 1984-1985. The percent deviation from the true values for the CAL ranged from 3.57%-6.49% for the two years, while that for all laboratories ranged from 19.19%-43.82%. Had the outliers been included in the all-participant data, the range would have been 28%-52%.

2. Illinois Environmental Protection Agency (IEPA)

In December 1981 the Analytical Chemistry Unit of the Illinois State Water Survey, of which the CAL laboratory is a part, received certification from the Illinois Environmental Protection Agency (IEPA). As part of the certification procedure, a team of reviewers from the

IEPA inspected the facilities and interviewed the staff to determine if the regulations set by the IEPA (18) were being followed. The IEPA also requires the analysis of performance evaluation samples containing the parameters for which certification is requested. Each laboratory is rated satisfactory or unsatisfactory for every analytical value it reports. Information regarding the true or expected values for the analytes present in the test samples is not made available to the participants. The CAL received a satisfactory rating for all values reported.

This certification was for chemical analysis of public water supply samples; however, the parameters that were certified included those found in precipitation, and the analytical methods were those used by the CAL. The CAL laboratory staff were among those interviewed and were responsible for much of the analytical data reported.

The certification was valid for two years, and recertification was requested in 1983 and again in 1985. After an on-site review of the laboratory, its staff, and the analytical methods being used, new Certificates of Approval were issued to the laboratory in December 1983 and July 1986.

3. Long Range Transport of Atmospheric Pollutants (LRTAP)

The Canadian Long Range Transport of Atmospheric Pollutants (LRTAP) program began interlaboratory comparability studies in December 1982 under the direction of the Quality Assurance and Methods Division of the National Water Research Institute (19). The first study in which the CAL participated was Study L4, which took place in August 1983. The CAL and 35 Canadian laboratories were asked to analyze 11 water samples that included natural waters, precipitation, and synthetic internal reference waters. Those parameters which were routinely analyzed by the participating laboratories were determined. Median concentrations for each parameter were selected from the data reported by all of the participating laboratories. These medians became the target values used to judge laboratory performance. Participants received a rating of satisfactory, moderate, or poor based on the percentage of results from that laboratory that were flagged for being biased high or low. The CAL has consistently received a satisfactory rating.

In 1984-1985, the CAL participated in six LRTAP intercomparison studies. Each study typically requested the participating labs to analyze 10 samples for those parameters routinely determined by the laboratory. In some of the intercomparisons, the samples were primarily surface waters with high ionic strengths. These samples often created problems with the analytical instruments at the CAL because they were unfiltered and frequently contained large amounts of particulate matter. Because these samples were not comparable to the precipitation samples the CAL routinely analyzed a simple screening protocol was established for the selection of samples in each LRTAP study that would be analyzed by the CAL staff. Samples that had a measured specific conductance >100 uS/cm, were highly colored, and/or contained large amounts of particulates were not analyzed by the CAL. For some studies this eliminated all but three samples from those the CAL analyzed. Tables 5 through 10 in Appendix D contain the CAL data and the Canada Center for Inland Waters (CCIW) medians for all of the samples analyzed by the CAL for LRTAP intercomparison studies of "Major Ions, Nutrients and Physical Properties in Water" in 1984 and 1985.

For each study, the participants received study summaries (19, 20, 21, 22) providing the data for all participants and the medians or target values used to assess laboratory performance. Samples considered to be biased high or low, were flagged and the percentage of flagged results was used to rank the participants in each study. Table VI-3 contains these percentages for the CAL as well as a mean percent flagged for all participants. A more detailed explanation of this calculation and the criteria used to determine bias in each study can be found in the project summaries listed in the references. Portions of Table VI-3 appeared in the ISWS 21st Progress Report to the Department of Energy (17).

Although the last published report (22) for these studies was issued for study L-9, summaries of all succeeding studies are available from the CCIW. The study summary for L-11 included a ranking of the

TABLE VI-3 Summary of Results from the Long Range Transport of Atmospheric Pollutants (LRTAP) Program Laboratory Intercomparison Studies.

Laboratory Study #	Date	Number of Participating Labs (n)	Average Score (%) [a]	
			All Labs	ISWS Lab
L-5	01/84	44	31.40	6.00
L-6	04/84	39	31.68	0.00
L-8	11/84	44	33.14	0.00
L-9	04/85	33	27.44	0.00
L-10	08/85	42	26.98	0.00
L-11	12/85	51	31.92	10.00

a. Average score equals the combined percent of results that were either flagged or biased. If all results were flagged and determined to be biased, a maximum score of 200% is possible.

participating laboratories based on their performance in studies 6, 8, 9, 10, and 11. The summary ranked 51 laboratories according to the accuracy of the data submitted. Of these 51 laboratories, only 25 (including the CAL) had participated in all 5 studies. The percentage of biased results for the combined studies was the criterion used to determine the laboratory ranking. The CAL was ranked first with an average score of 2.0%. The mean score for all 51 laboratories was 34.6%. Examination of the CAL data in Table VI-3 shows that the CAL results are consistently characterized by a lack of bias for all of these LRTAP studies (22). As with the summary results from the WMO intercomparisons, the CAL scores on the LRTAP studies indicate that consistency and a lack of bias are typical for the CAL results.

4. European Monitoring and Evaluation Program (EMEP)

The third international program that the CAL participated in during this time period was sponsored by the Norwegian Institute for Air Research in Lillestrom, Norway. Designated the EMEP, this project is designed to assess the comparability of analytical methods in use by European laboratories conducting research in the area of acidic deposition. This program is a cooperative effort of the United Nations Economic Committee for Europe as a part of the monitoring and evaluation of the long range transport of air pollutants in that region (23).

Four synthetic precipitation samples containing known amounts of sulfate, nitrate, ammonium, strong acid, magnesium, sodium, chloride, calcium, and potassium were provided to each laboratory participating in this study, with the results forwarded to the Norwegian Institute for compilation and data reporting. Supporting methods documentation and quality assurance protocols in use at each facility were also provided. The CAL laboratory was first invited to participate in this program in 1984. A summary of the CAL measured results compared with the expected concentrations is presented in Table VI-4. No data on the performance of the CAL laboratory relative to the rest of the EMEP participants is available; however, the mean percent deviation of the CAL results was approximately 4%. This value is consistent with the mean percent deviations reported for the WMO and LRTAP intercomparisons.

Continued participation in interlaboratory comparisons such as this is an integral part of the CAL's quality assurance program. In addition to providing an independent assessment of the accuracy of our laboratory measurements, the methods documentation supplied with the analytical results forms a data base that can be used by all participants to compare their methodologies to those used by other laboratories.

TABLE VI-4 EMEP Study #8 Interlaboratory Comparison Study April 1984 - CAL Reported Values Compared to EMEP Expected Values.

	Sample Number							
	G1		G2		G3		G4	
Parameter	**EMEP**	**CAL**	**EMEP**	**CAL**	**EMEP**	**CAL**	**EMEP**	**CAL**
Calcium (mg/L)	0.97	0.962	0.58	0.577	0.46	0.461	0.89	0.884
Magnesium (mg/L)	0.46	0.444	0.40	0.386	0.10	0.097	0.08	0.077
Sodium (mg/L)	1.57	1.54	3.59	3.44	3.99	3.84	1.80	1.76
Potassium (mg/L)	0.43	0.429	0.52	0.505	0.22	0.213	0.17	0.172
Ammonium (mg/L)	0.31	0.27	0.26	0.22	1.12	1.11	1.40	1.37
Nitrate + Nitrite (mg/L)	4.25	4.24	2.43	2.44	2.08	2.07	4.82	4.82
Chloride (mg/L)	2.33	2.32	2.13	2.13	2.69	2.69	3.14	3.15
Sulfate (mg/L)	5.09	4.67	7.82	7.70	8.51	8.39	5.48	5.18
pH (units)	4.24	4.28	4.78	4.78	4.88	4.85	4.16	4.18
Specific Conductance (uS/cm)	44.0	46.6	35.6	38.3	38.3	41.0	52.7	56.1

VII. SUMMARY

When first organized, the NADP established as one of its primary goals the production of analytical data which were of the highest quality. To achieve this end, the NADP Quality Assurance Plan-Deposition Monitoring (2) was developed in 1984 to clearly define the guidelines for field, laboratory, and data management operations. This QA Plan also fully documents the requirements of the network for all three areas of operation.

The CAL was directed to produce data whose precision and bias were quantified. Minimum method detection limits were established for all analytical parameters, and limits for variance in accuracy were defined. Finally, complete documentation of all quality assurance procedures in use at the CAL was required as well as annual reports of the information derived from the quality assurance data.

The QA Report for 1978-1983 (1) described the early stages in the development of the CAL laboratory quality assurance program. The present report continues that documentation by detailing the refinements to the program that occurred during 1984 and 1985. Suggestions from members of NADP/NTN Subcommittee 2 on Quality Assurance were integral to this continued development, as were the guidelines set forth in the QA Plan.

The data presented in this report indicate that the CAL has been successful in meeting the network requirements as detailed in the QA Plan (2). The analytical bias and precision tables in Section IV show that the desired limits for variance in accuracy were achieved. The MDLs listed in Table II-1 meet or exceed those listed in the QA Plan. The initiation of an internal blind program, coupled with the changes to the replicate analysis procedures, provide the data user with additional information for assessing the quality of the CAL data. The data that result from these new procedures provide a truer indication of the quality of the network sample data than did the information obtained from the analysis of internal reference samples alone. Confirmation of the CAL data quality is provided by the CAL's performance in several interlaboratory performance studies. Table VII-1 highlights the changes that have occurred to the laboratory quality assurance program.

The analytical methods manual (3) that became available in 1986 documents all the laboratory procedures used to analyze the network samples. This report in conjunction with the one published in 1987 (1) provides documentation of the procedures and the data produced for the laboratory quality assurance program through 1985. The CAL, in conjunction with the NADP/NTN Quality Assurance Manager and the Coordinator's Office, is currently working to provide quality assurance data in a more timely manner, thus meeting all of the goals of the Quality Assurance Plan.

TABLE VII-1 Changes to the Laboratory Quality Assurance Program.

A. Documentation of Standard Operating Procedures
- 1984-1985 - Development of analytical methods manual (includes new method for calculating MDL).
- 1987 - Publication of Quality Assurance Report for 1978-1983 (March).

B. Change in Analytical Methods
- 1985 - Analysis of sulfate, nitrate, and chloride ions changed from automated wet chemical methods to ion chromatography resulting in minor changes in the MDLs for the three ions (May).

C. New Facilities
- 1985 - Move to new facilities results in improved laboratory, office, and storage areas; equipment to maintain a clean air environment installed in the laboratories; new deionizing system installed; walk-in coolers available for sample and supplies storage (November).

D. Laboratory Blanks
- 1982 - Dishwasher installed to wash buckets; city tap water used for wash cycle with DI water rinse (May).
- 1984 - Dishwasher replumbed to use only DI water for all cycles (November).
- 1984 - pH and specific conductance measured for all blank samples (January).
- 1984-1985 - Special bucket blank studies performed to investigate both prolonged and normal exposure of acidic solutions and prolonged exposure of DI water to the sample containers.

TABLE VII-1 (concluded) Changes to the Laboratory Quality Assurance Program.

E. Analytical Bias and Precision
  1984 - O/Q replicate split analyses begun (July).
  1984 - Internal blind sample program begun (July).

F. Reanalysis
  1981 - Criteria for IPD and CPD established (October).
  1987 - Factors used to calculate conductivity changed (March).

G. Interlaboratory Comparisons
  1980 - First CAL participation in WMO intercomparisons.
  1981 - Certification as an environmental laboratory granted by IEPA; recertification obtained in 1983 (December) and 1986 (July).
  1982 - USGS interlaboratory comparisons begun
  1983 - First CAL participation in LRTAP interlaboratory comparability studies (August).
  1984 - First CAL participation in EMEP studies (April).

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22. __________, G. Dookhran, P. Leishman, and S. Todd: LRTAP Intercomparison Study L9: Major Ions, Nutrients and Physical Parameters in Water; National Water Research Institute; Burlington, Ontario; August 1985.

23. Hanssen, J. E., and N. E. Ladegard: The Seventh Intercomparison of Analytical Methods Within the EMEP; EMEP/CCC Report 1/84; Norwegian Institute for Air Research; February 1984.

APPENDIX A

Glossary of Terms

GLOSSARY OF TERMS

Term	Abbreviation	Definition
Accuracy		The difference between the mean value and the true value when the latter is known or assumed. The concept of accuracy includes both bias (systematic error) and precision (random error).
Bias		A persistent positive or negative deviation of the measured value from the true value due to the experimental method. In practice, it is expressed as the difference between the mean value obtained from repetitive analysis of a homogenous sample and the accepted true value. Bias = measured value - true value
Critical Percent		A calculated percent used to determine if the measured bias is or is not statistically significant. It is calculated from the formula: $\text{critical \%} = \frac{s_{sp} - t_{0.95,(n1 + n2)-2}}{\overline{x}_{true}} \times 100$ where: $s_{sp} = \sqrt{\frac{s^2_{true}}{n_{true}} + \frac{s^2_{measured}}{n_{measured}}}$ and: s = standard deviation n = number of values $t_{0.95,(n1 + n2)-2}$ = t statistic at the 95% confidence level and (n1 + n2)-2 degrees of freedom

External Blind Sample		A quality assurance sample of known analyte concentrations submitted to the CAL by an external agency. These samples arrive in normal sample containers and undergo routine processing and analysis. The fact that the sample was not a routine sample is not known by the CAL until all analyses are complete. Data from the analysis of these samples can be used to assess the potential for contamination of the network samples through routine field and laboratory handling procedures.
Internal Blind Sample		A quality assurance sample of known analyte concentrations submitted for sample processing and routine analysis by the Laboratory Quality Assurance Specialist. The fact that these samples are blinds is known only to the processing staff. The expected analyte concentrations are unknown to both the processing staff and the analysts. Data from the analysis of these samples provide another means of assessing laboratory bias and precision.
Laboratory Spike		A known volume of analyte added to one portion of a replicate or split sample. The concentration of the added analyte should approximate that found in the unspiked sample. The difference in analyte concentration between the spiked and unspiked samples is used to determine the percent recovery. These samples are used in methods development and comparisons and provide an estimate of the accuracy of the methods selected for analysis.
Mean	$\overline{x}$	$\overline{x} = \sum_{i=1}^{n} x_i/n$

Mean Bias		$\frac{\sum \text{bias for each sample}}{\text{total number of replicates (n)}}$
Mean Percent Recovery		$\frac{\sum \text{percent recovery for each sample}}{\text{total number of replicates (n)}}$
Method Detection Limit	MDL	The minimum concentration of an analyte that can be reported with 99% confidence that the value is above zero. The MDL is operationally defined as: $MDL = (s)t_{n-1,1-\alpha = 0.99)}$ where: s = standard deviation of repetitive measurements (≥ 7) of a solution containing the analyte at a concentration near the estimated MDL. $t_{n-1,1-\alpha = 0.99)}$ = student's t value for a one-tailed test appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom.
Percent Bias		The difference between the mean value obtained by repeated analysis of a homogenous sample and the accepted true value expressed as a percentage of the true value: $\% \text{ Bias} = 100 \times [(V_m - V_t)/V_t]$ where: V_m = measured value V_t = true value
Percent Recovery		An estimate of the bias of an analytical method determined from analyte spikes of natural samples. The percent recovery is calculated as: $\% \text{ Recovery} = 100 \text{ X } [(a-b)/c]$ where: a = measured concentration of spiked sample

		b = measured concentration of unspiked sample c = calculated spike concentration
Precision		The degree of agreement of repeated measurements of a homogenous sample by a specific procedure, expressed in terms of dispersion of the values obtained about the mean value. It is often reported as the sample standard deviation (s).
Quality Assessment		The system of procedures that ensures that quality control practices are achieving the desired goal in terms of data quality. This includes continuous evaluation of analytical performance data.
Quality Assurance Program		A program designed to reduce measurement error to tolerable limits and provide the means of ensuring data validity. This includes both quality control and quality assessment activities.
Quality Control	QC	The system of procedures designed to eliminate analytical error. These procedures determine potential sources of sample contamination and monitor analytical procedures to produce data within prescribed tolerance limits.
Quality Control Check Sample	QCS	A sample containing known concentrations of analytes . The laboratory uses this sample to routinely demonstrate that it can obtain acceptable results with procedures being used to analyze wet deposition samples. Analyte true values are known by the analyst.

Relative Standard Deviation	RSD	The standard deviation expressed as a percentage. $RSD = 100 \times (s/\bar{x})$ where: s = sample standard deviation $\bar{x}$ = mean value
Replicates (Splits)		Two aliquots of the same sample treated identically throughout a laboratory analytical procedure. Analyses of laboratory replicates indicate the precision associated with laboratory procedures but not with sample collection and field handling (processing). These samples may also be referred to as splits.
Sensitivity		The method signal response per unit of analyte.
Standard Deviation	s	A number that represents the dispersion of values around their mean, calculated as: $s = \sqrt{\frac{\sum (x_i - \bar{x})^2}{n - 1}}$ where: x_i = each individual value $\bar{x}$ = average of all values n = number of values

APPENDIX B

Laboratory Blanks
Plots and Tables
1984-1985

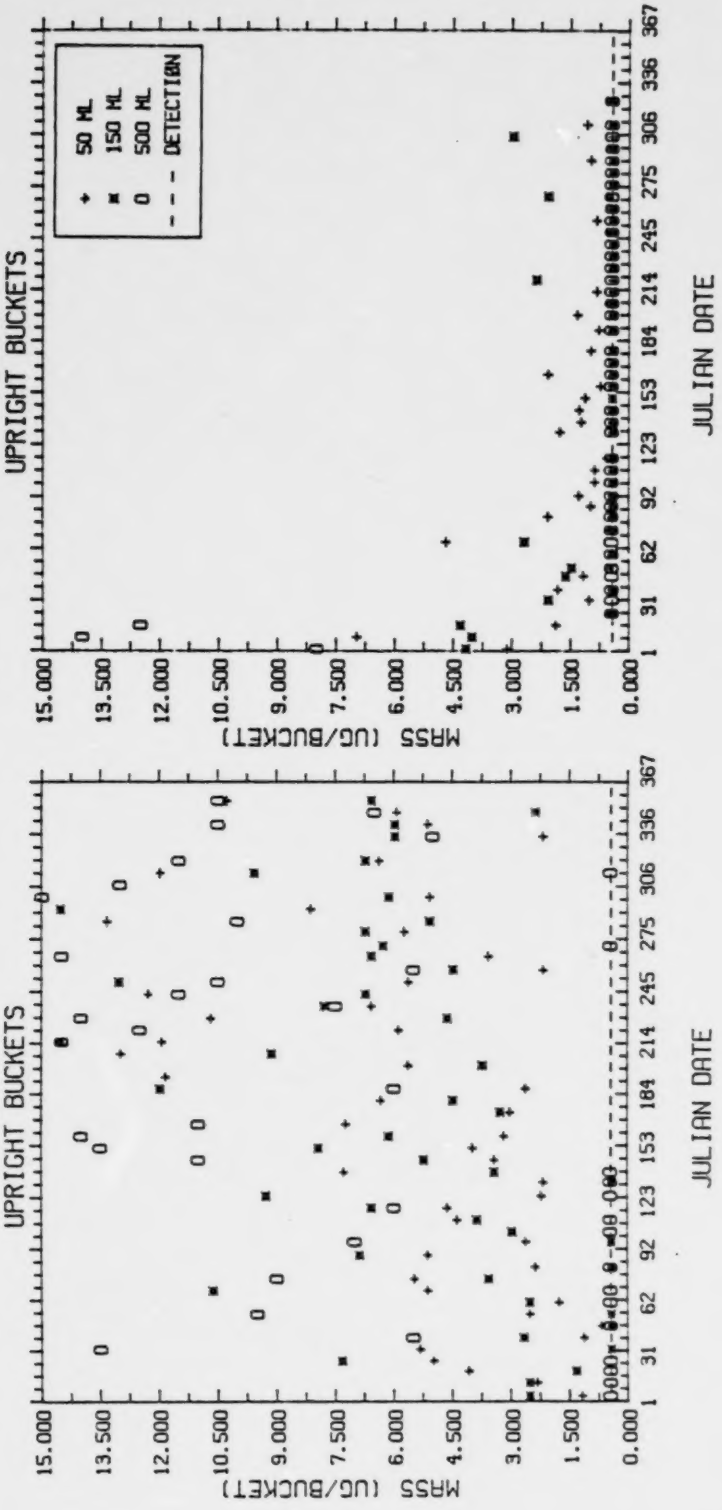


FIGURE 1. Measured calcium mass in upright bucket blanks for 1984 and 1985.

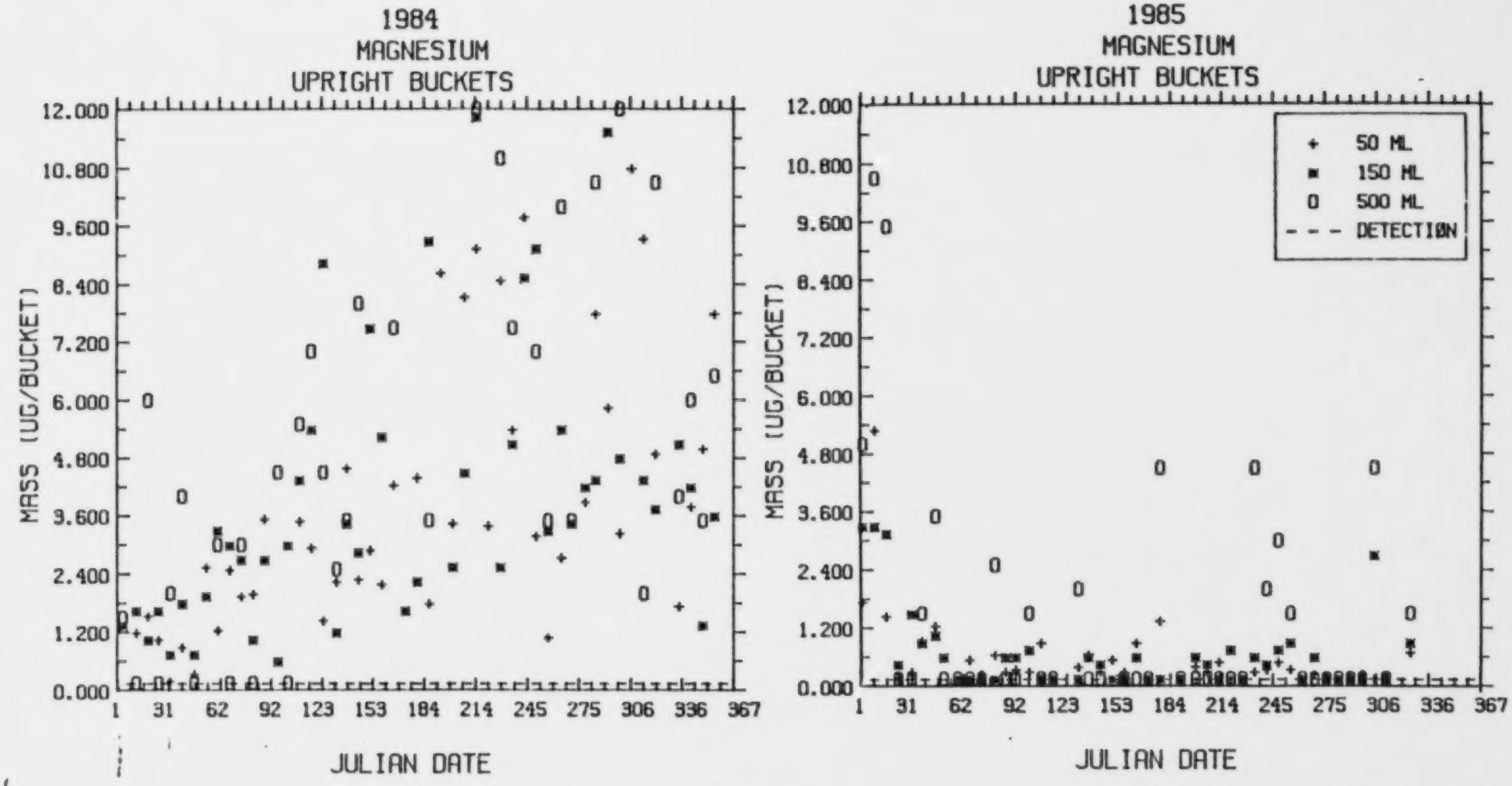


FIGURE 2. Measured magnesium mass in upright bucket blanks for 1984 and 1985.

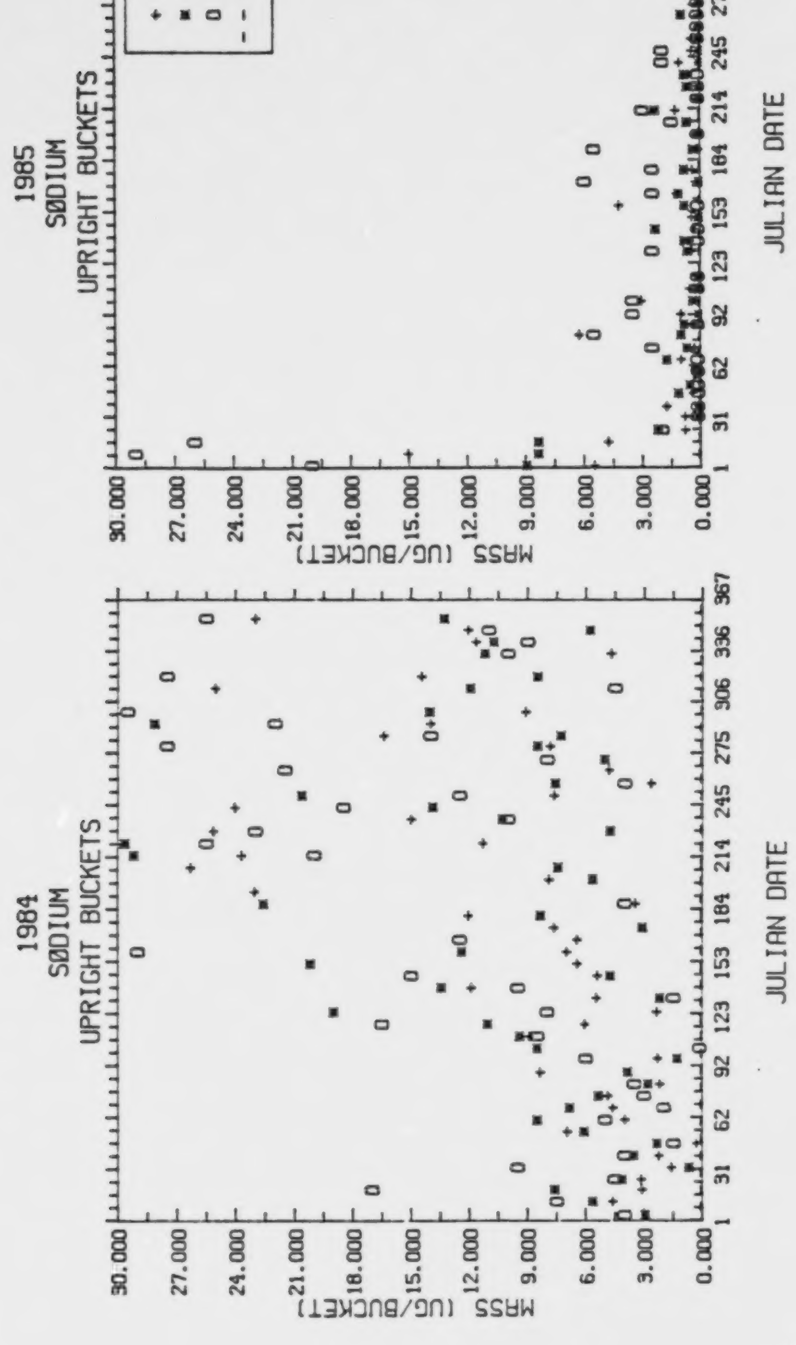


FIGURE 3. Measured sodium mass in upright bucket blanks for 1984 and 1985.

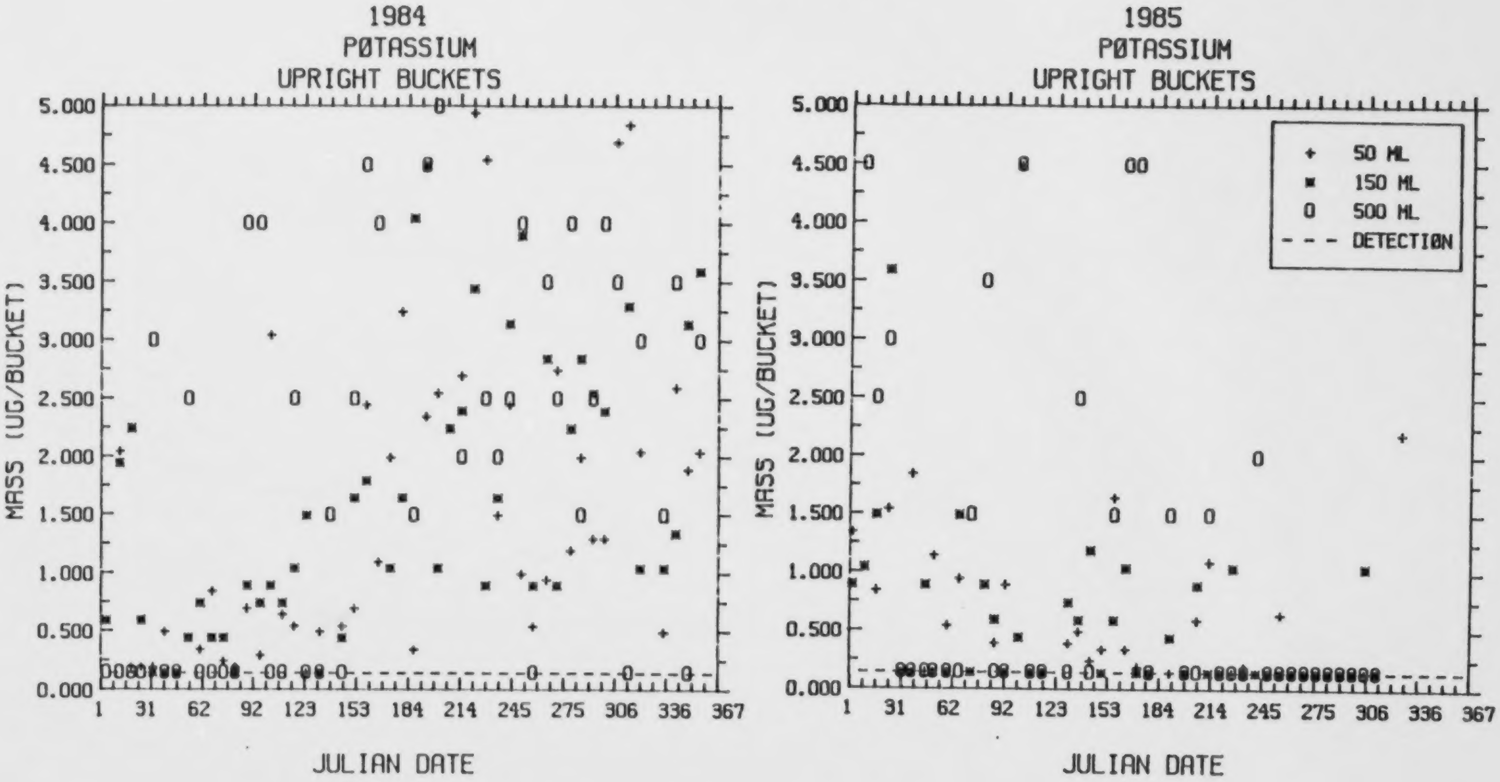


FIGURE 4. Measured potassium mass in upright bucket blanks for 1984 and 1985.

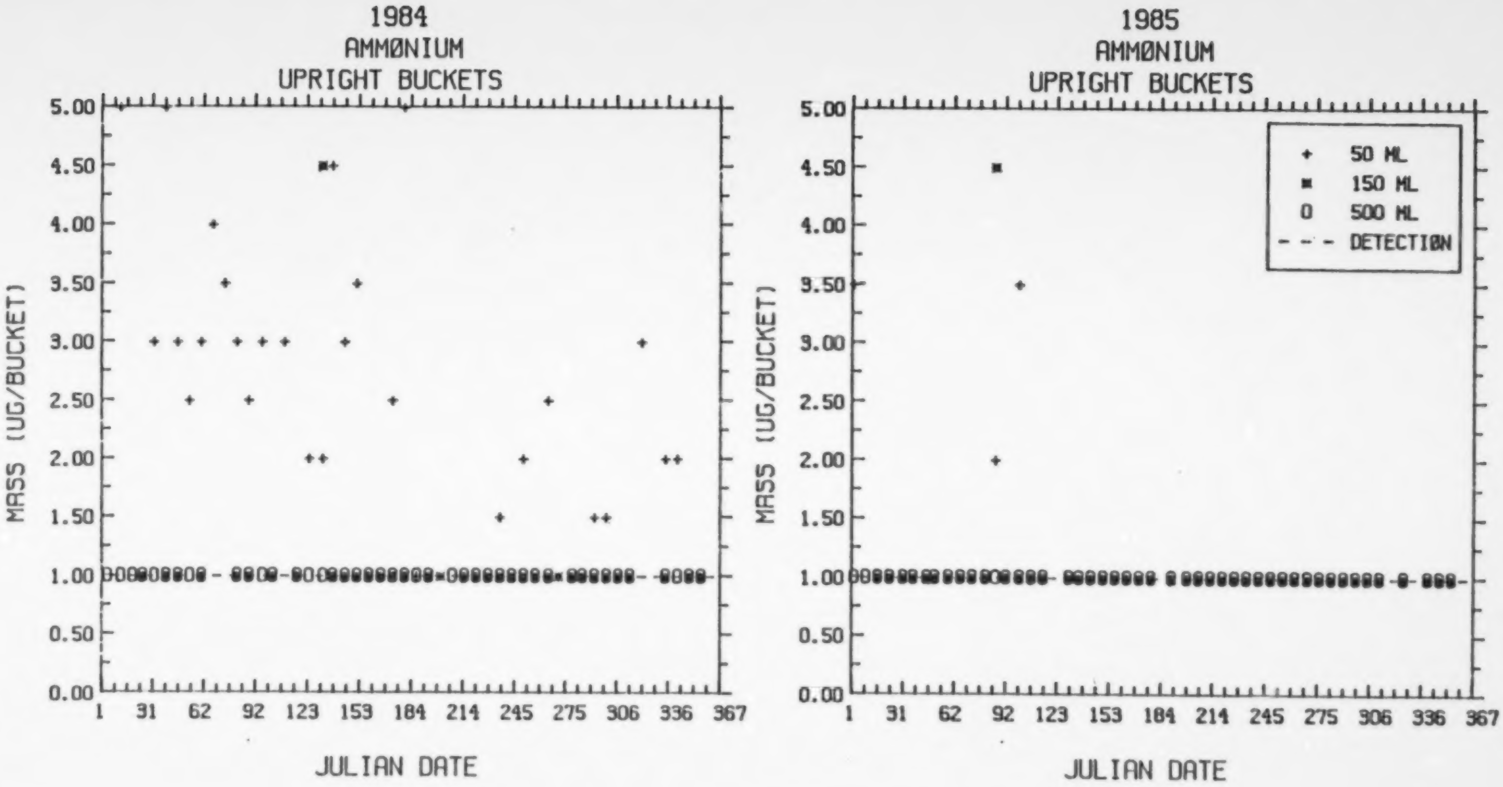


FIGURE 5. Measured ammonium mass in upright bucket blanks for 1984 and 1985.

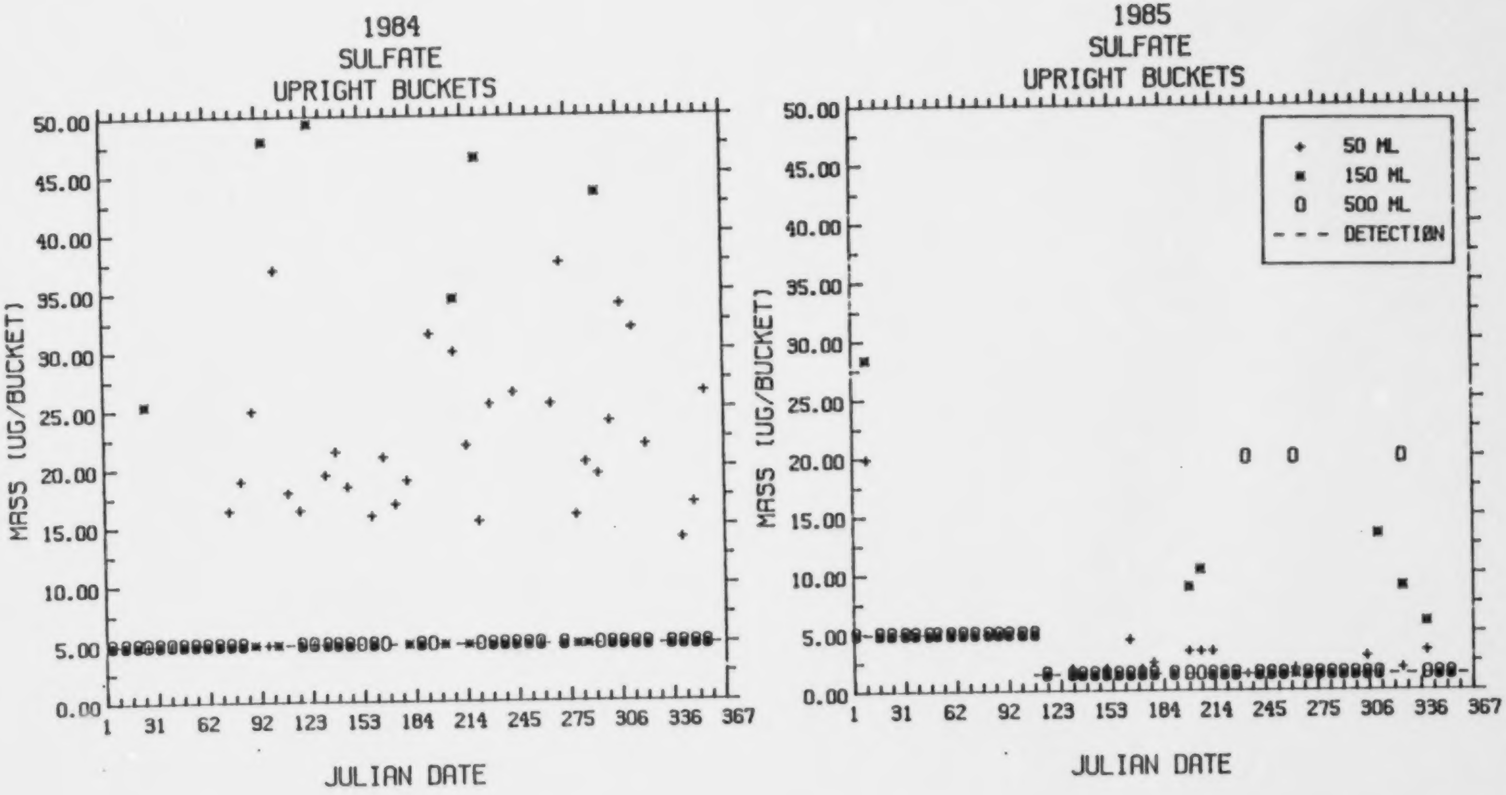


FIGURE 6. Measured sulfate mass in upright bucket blanks for 1984 and 1985.

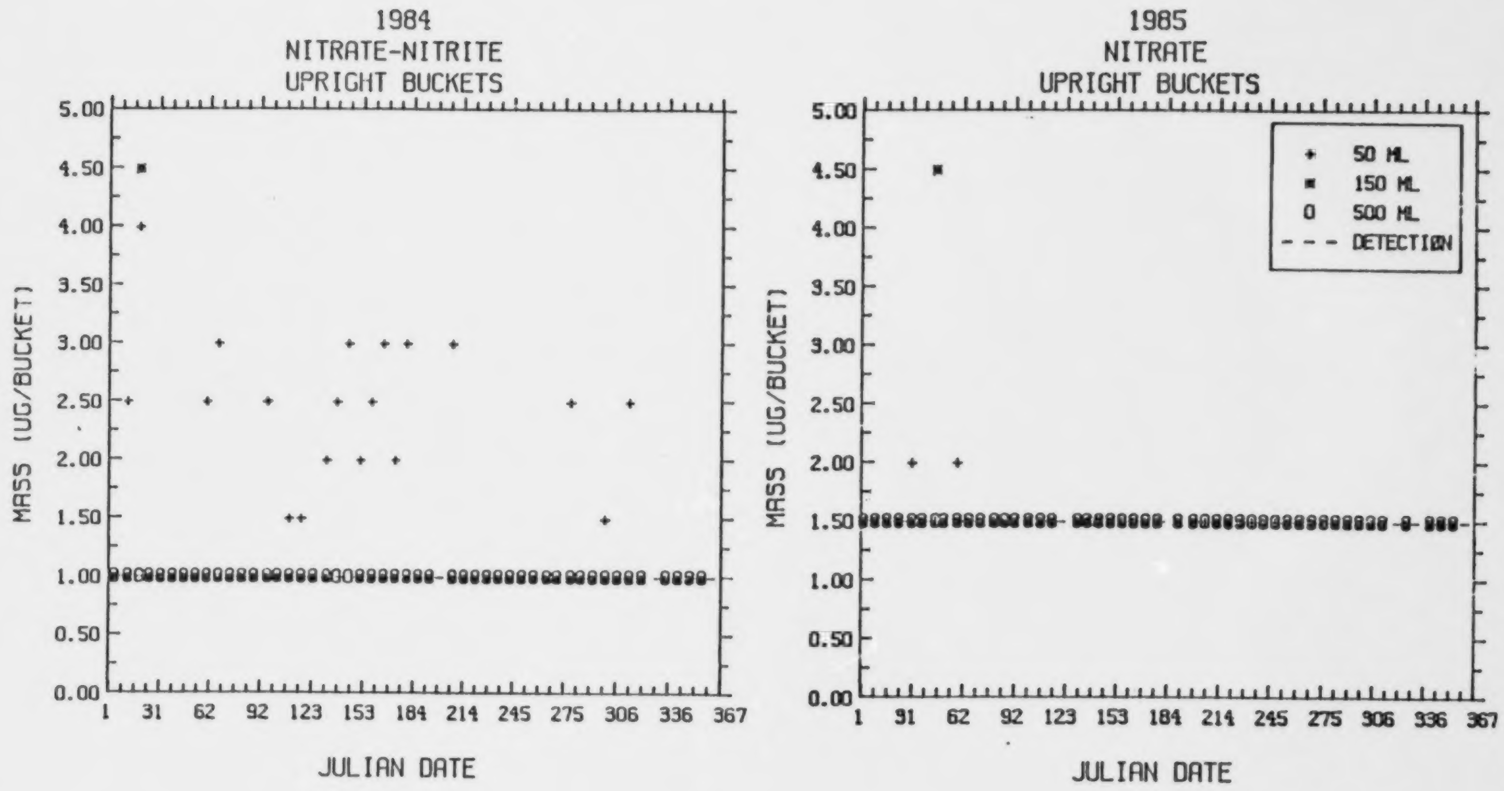


FIGURE 7. Measured nitrate-nitrite mass in upright bucket blanks for 1984 and measured nitrate mass in upright bucket blanks for 1985.

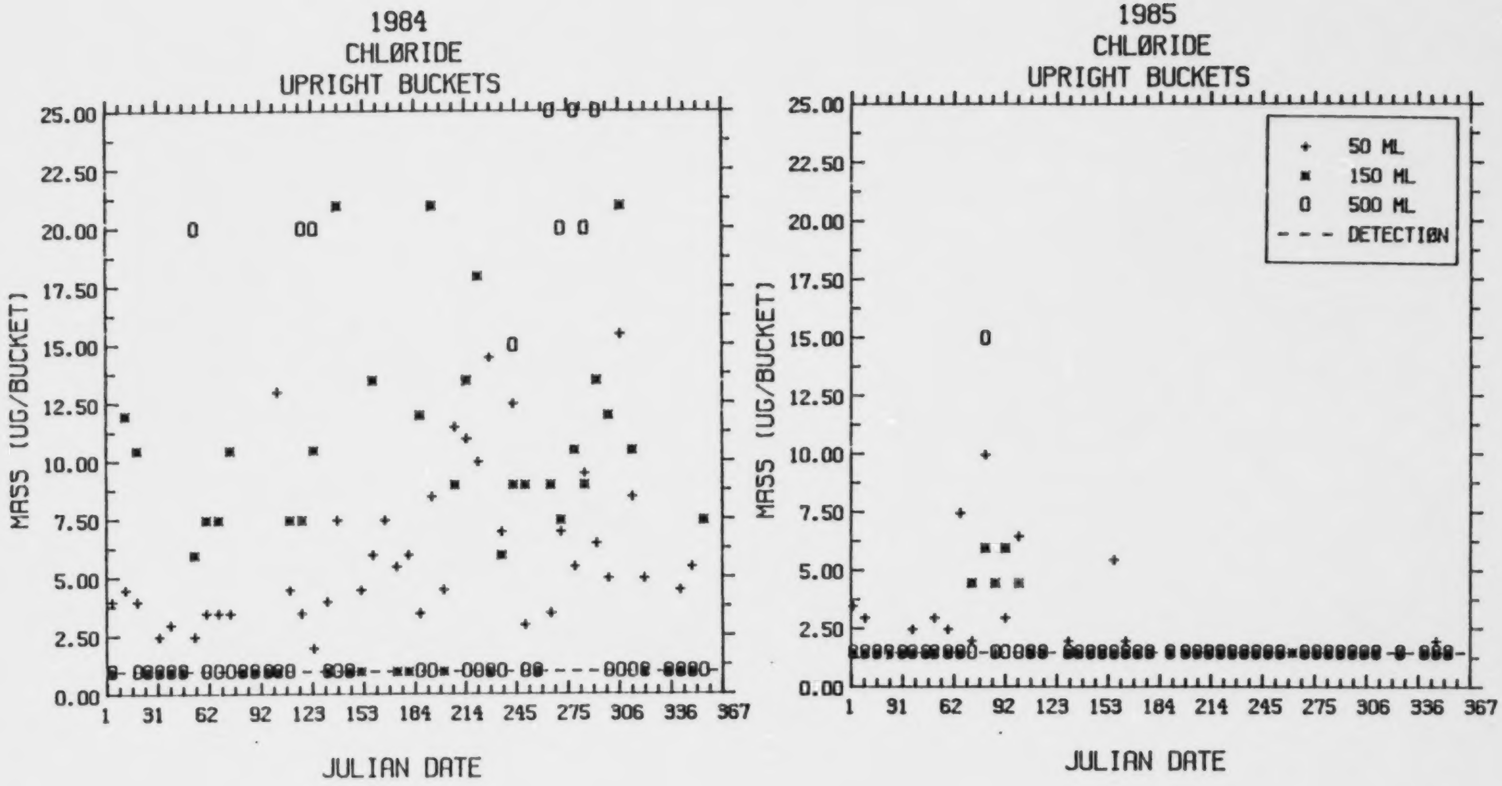


FIGURE 8. Measured chloride mass in upright bucket blanks for 1984 and 1985.

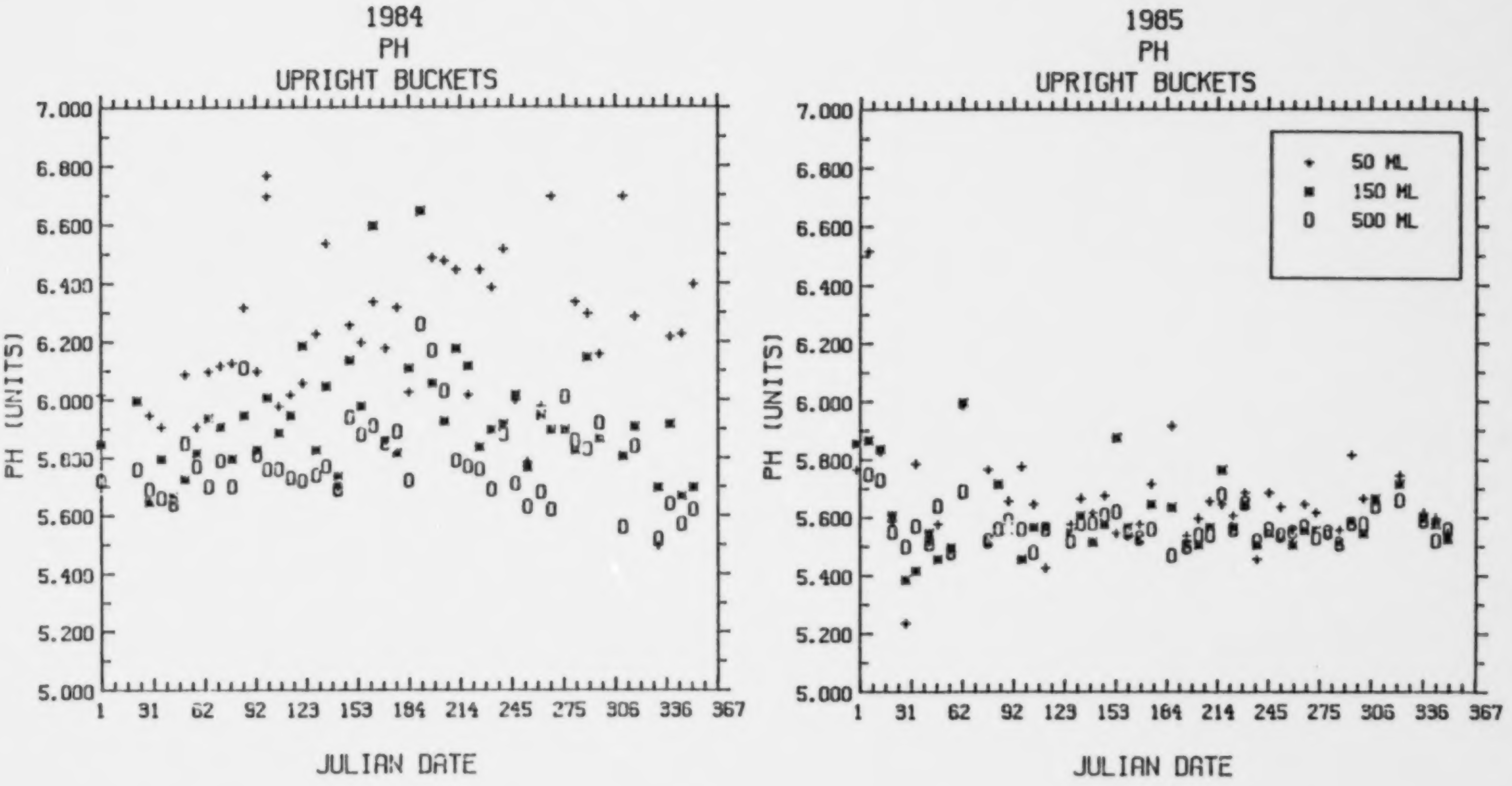
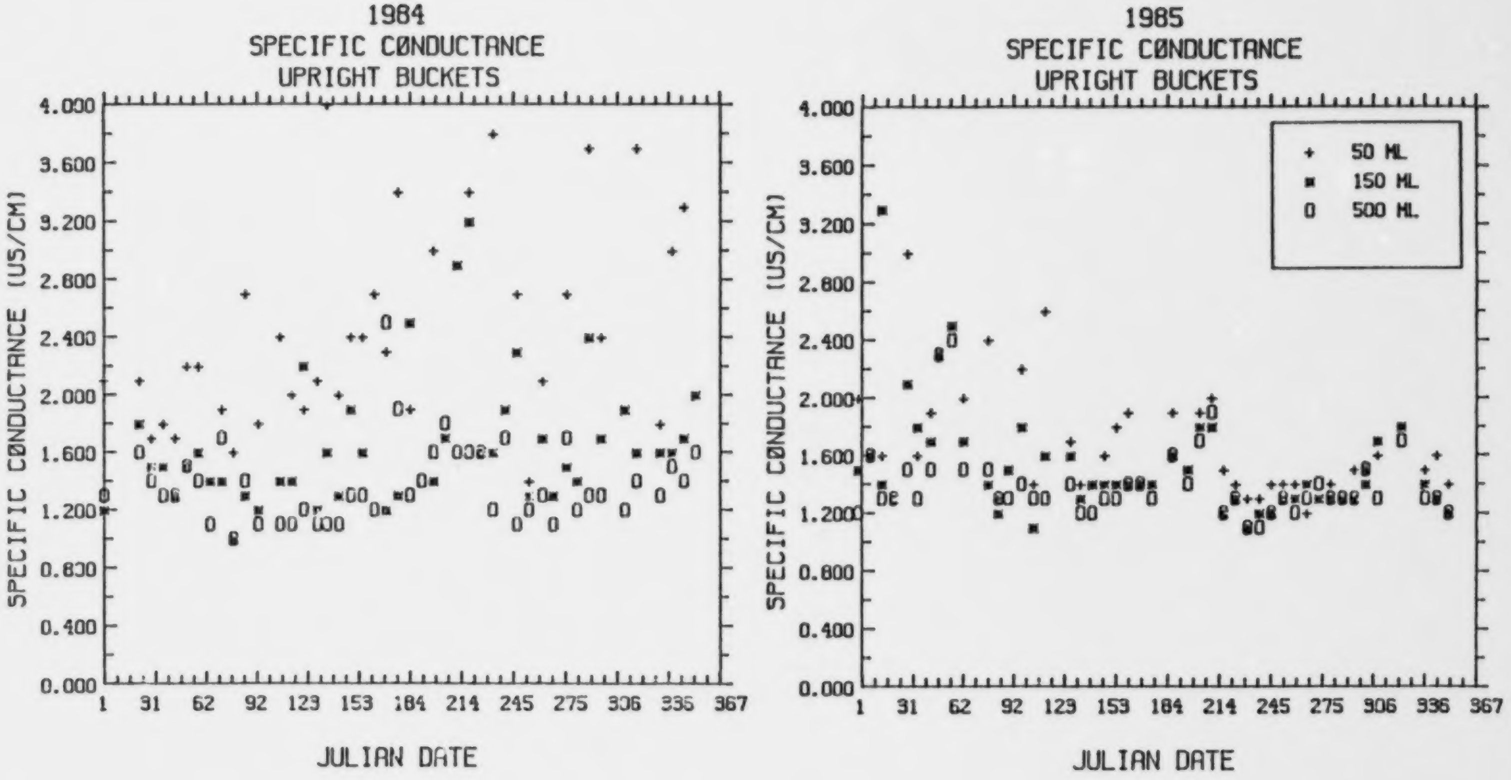


FIGURE 9. Measured pH in upright bucket blanks for 1984 and 1985.



1984
SPECIFIC CØNDUCTANCE
UPRIGHT BUCKETS

1985
SPECIFIC CØNDUCTANCE
UPRIGHT BUCKETS

FIGURE 10. Measured specific conductance in upright bucket blanks for 1984 and 1985.

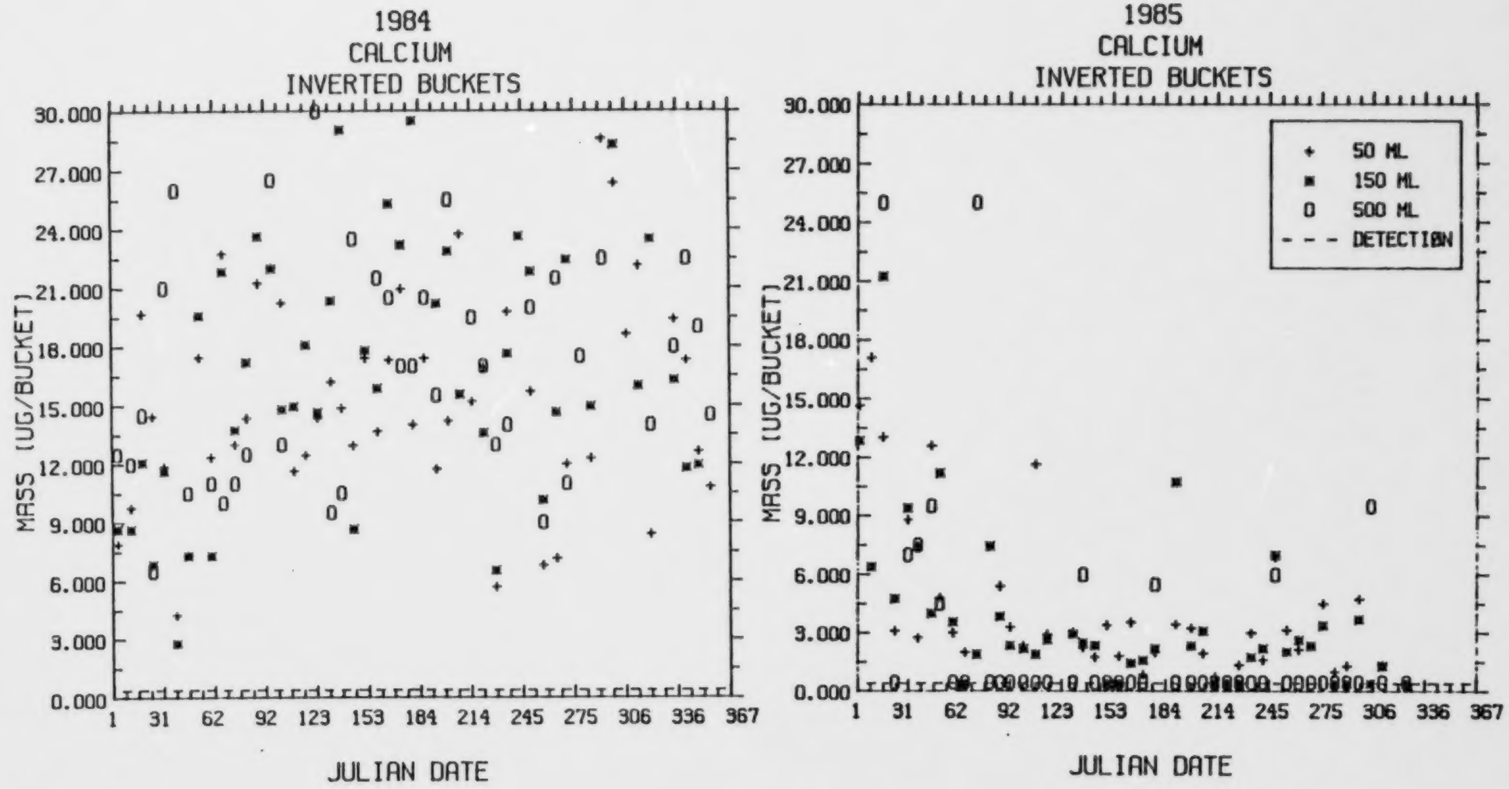


FIGURE 11. Measured calcium mass in inverted bucket blanks for 1984 and 1985.

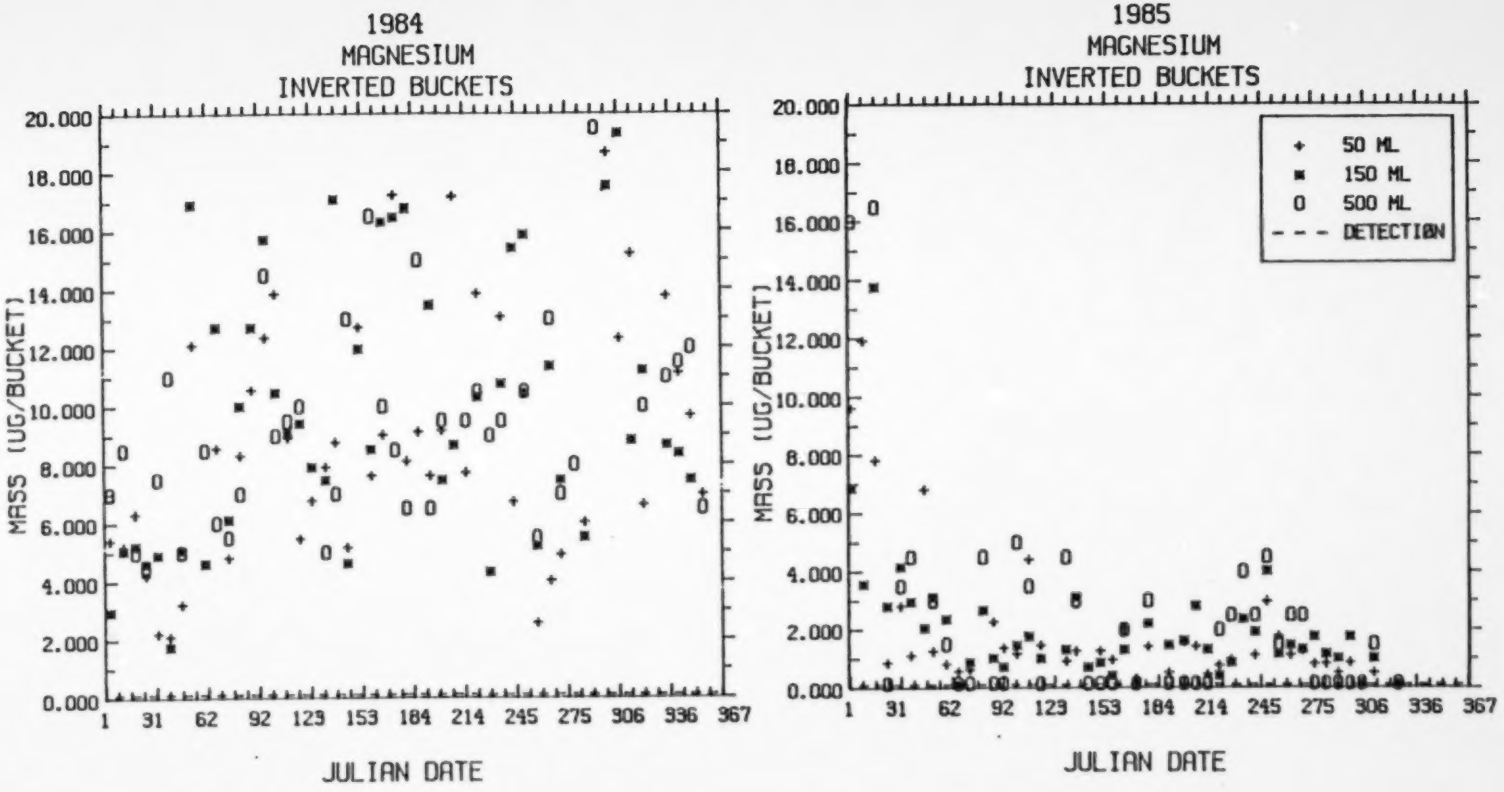


FIGURE 12. Measured magnesium mass in inverted bucket blanks for 1984 and 1985.

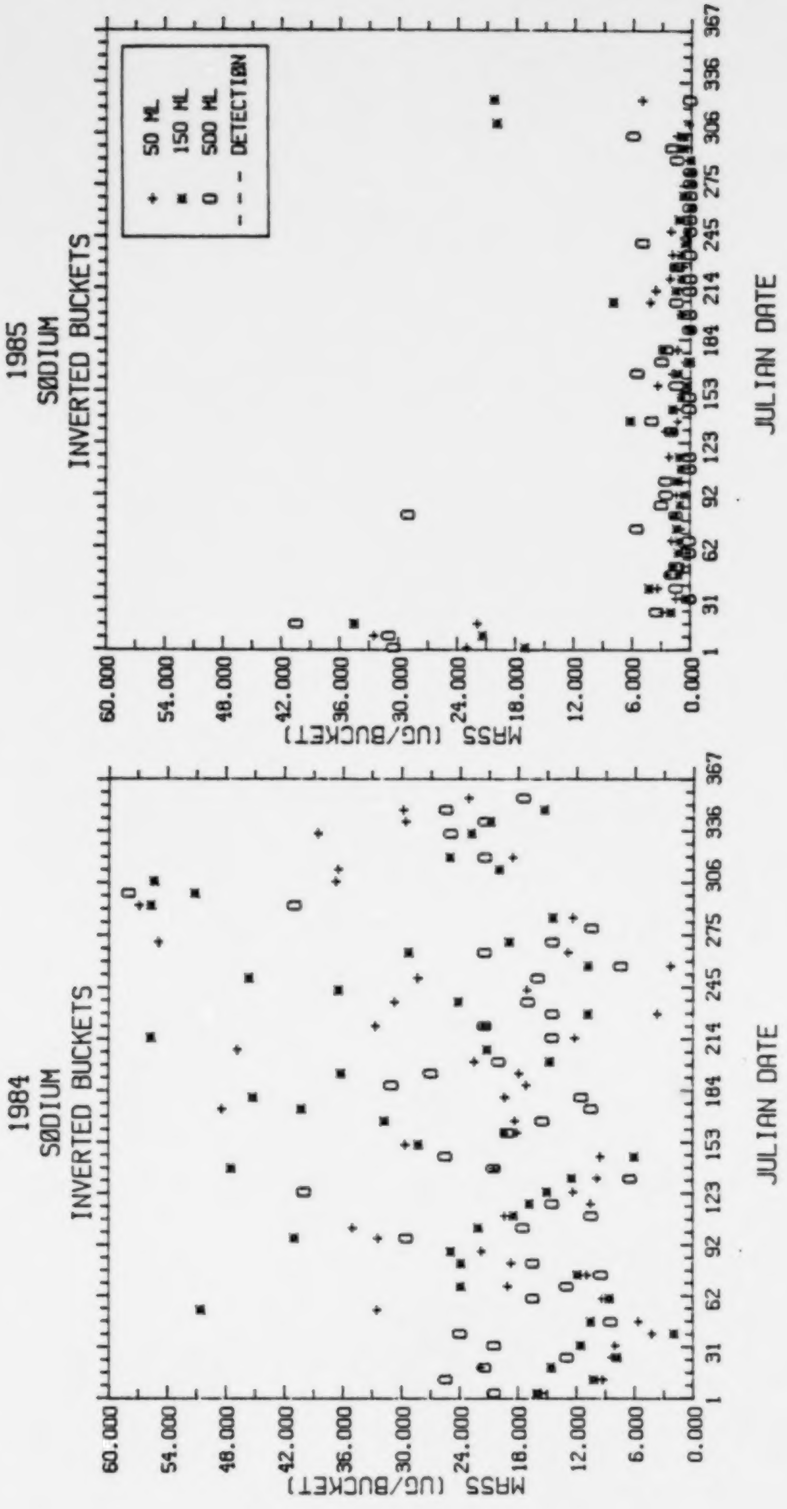


FIGURE 13. Measured sodium mass in inverted bucket blanks for 1984 and 1985.

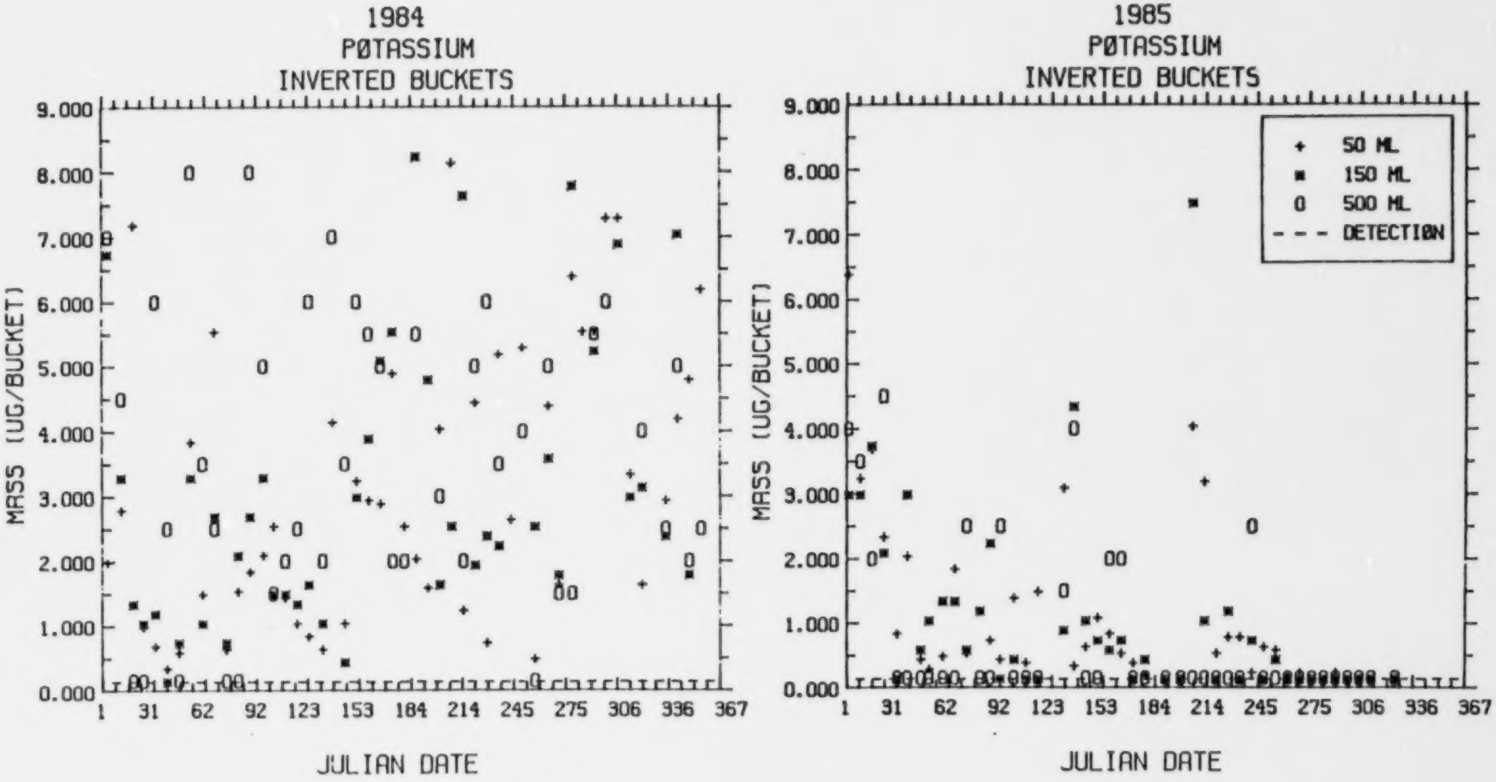


FIGURE 14. Measured potassium mass in inverted bucket blanks for 1984 and 1985.

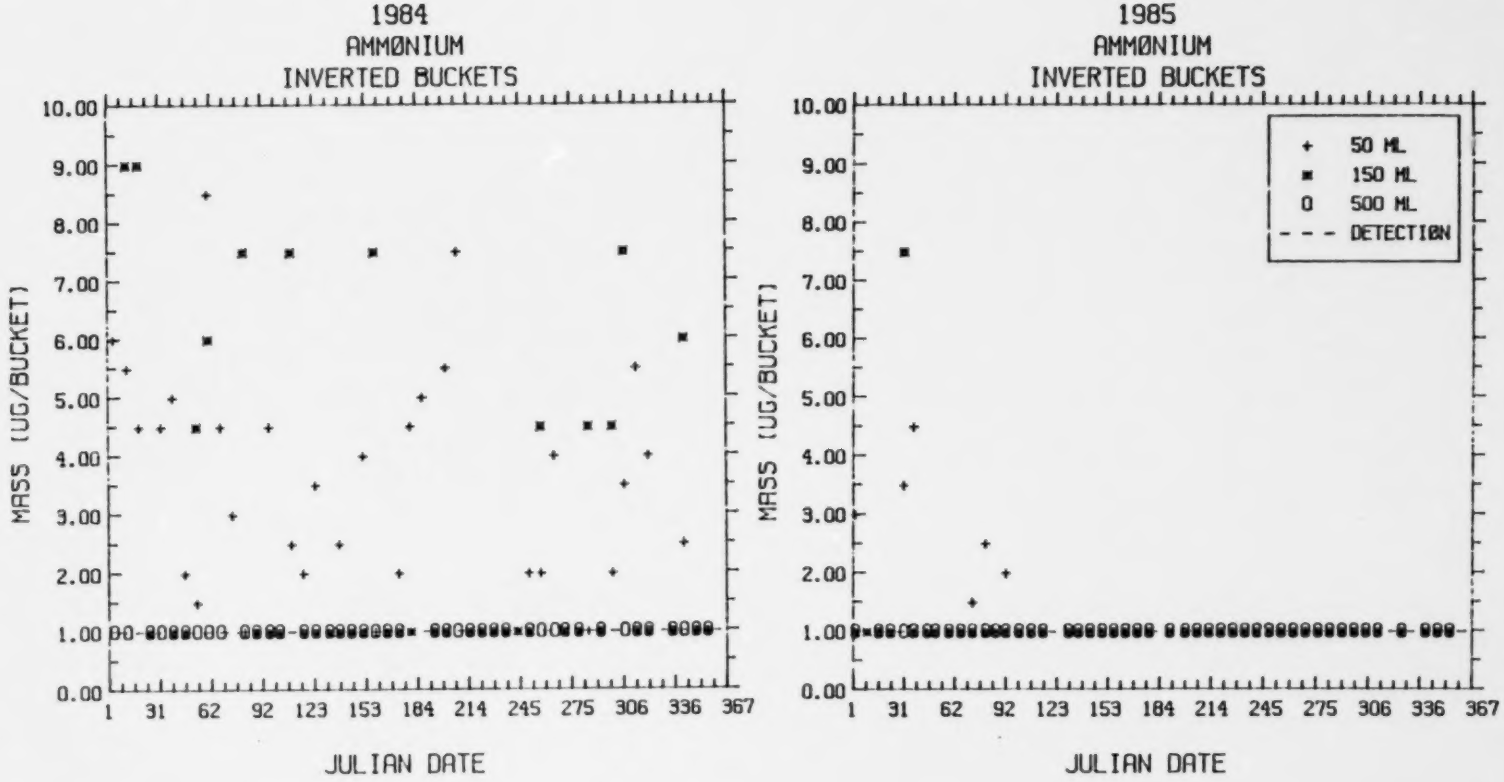


FIGURE 15. Measured ammonium mass in inverted bucket blanks for 1984 and 1985.

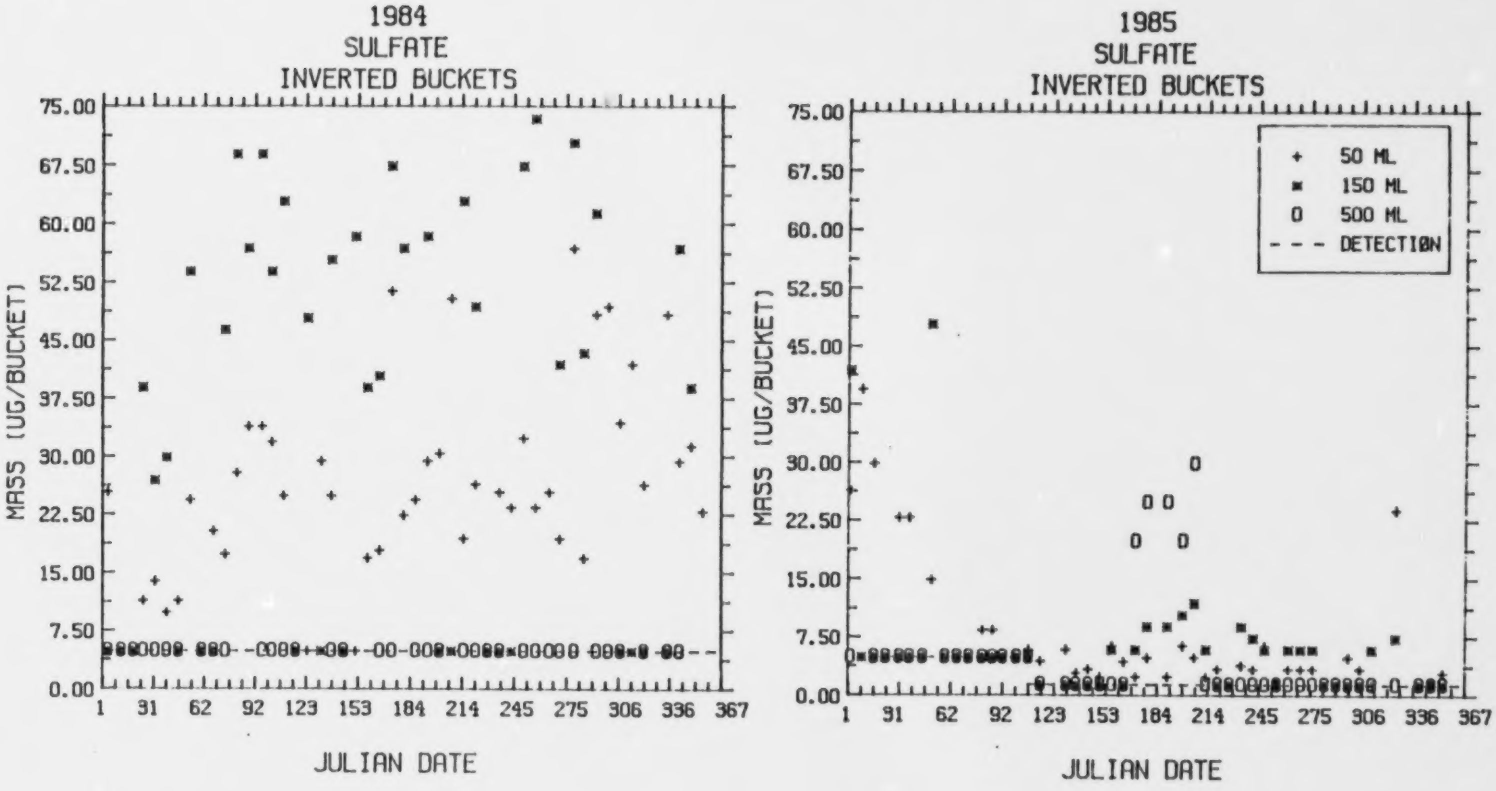


FIGURE 16. Measured sulfate mass in inverted bucket blanks for 1984 and 1985.

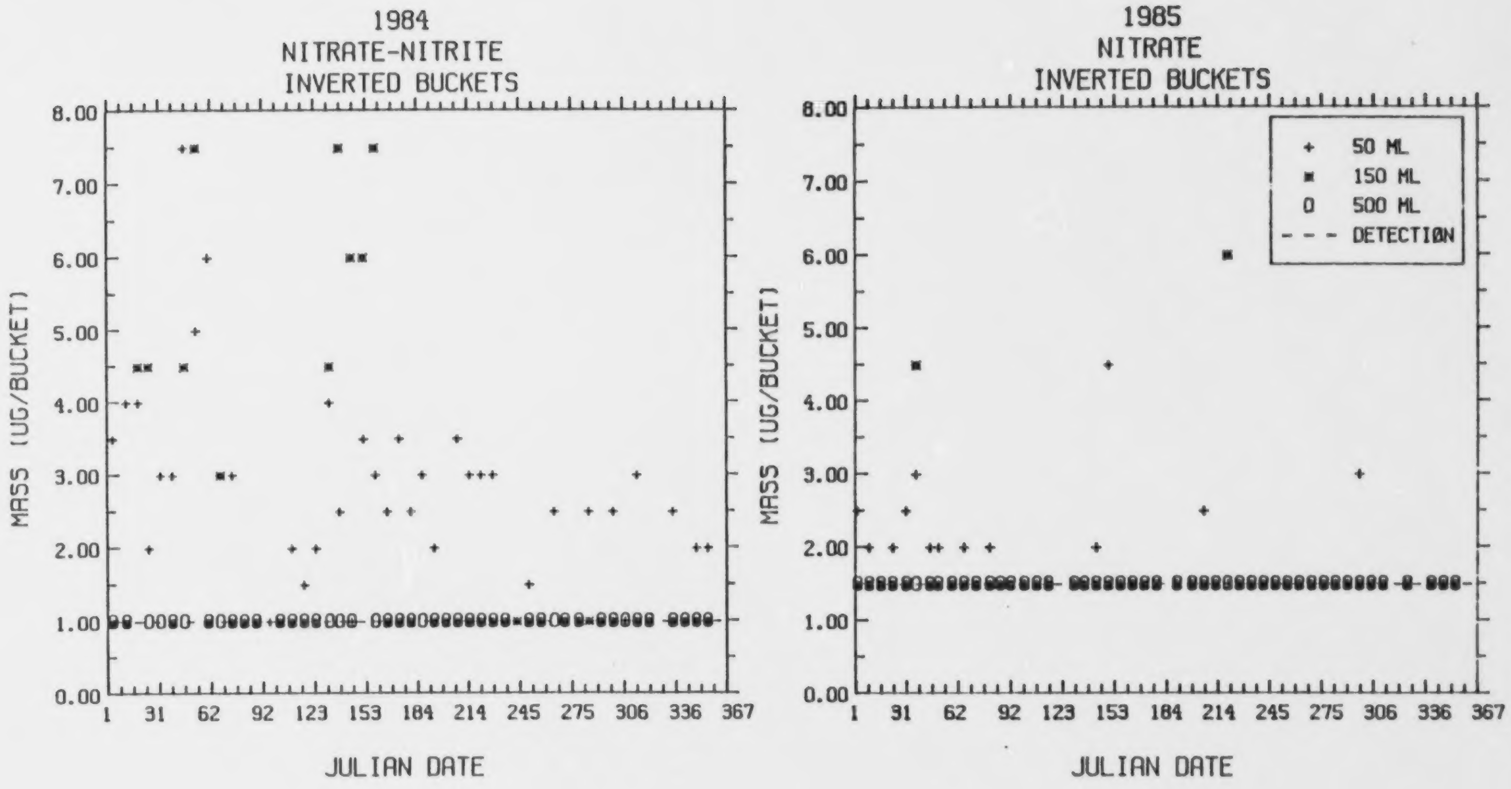


FIGURE 17. Measured nitrate-nitrite mass in inverted bucket blanks for 1984 and measured nitrate mass in inverted bucket blanks for 1985.

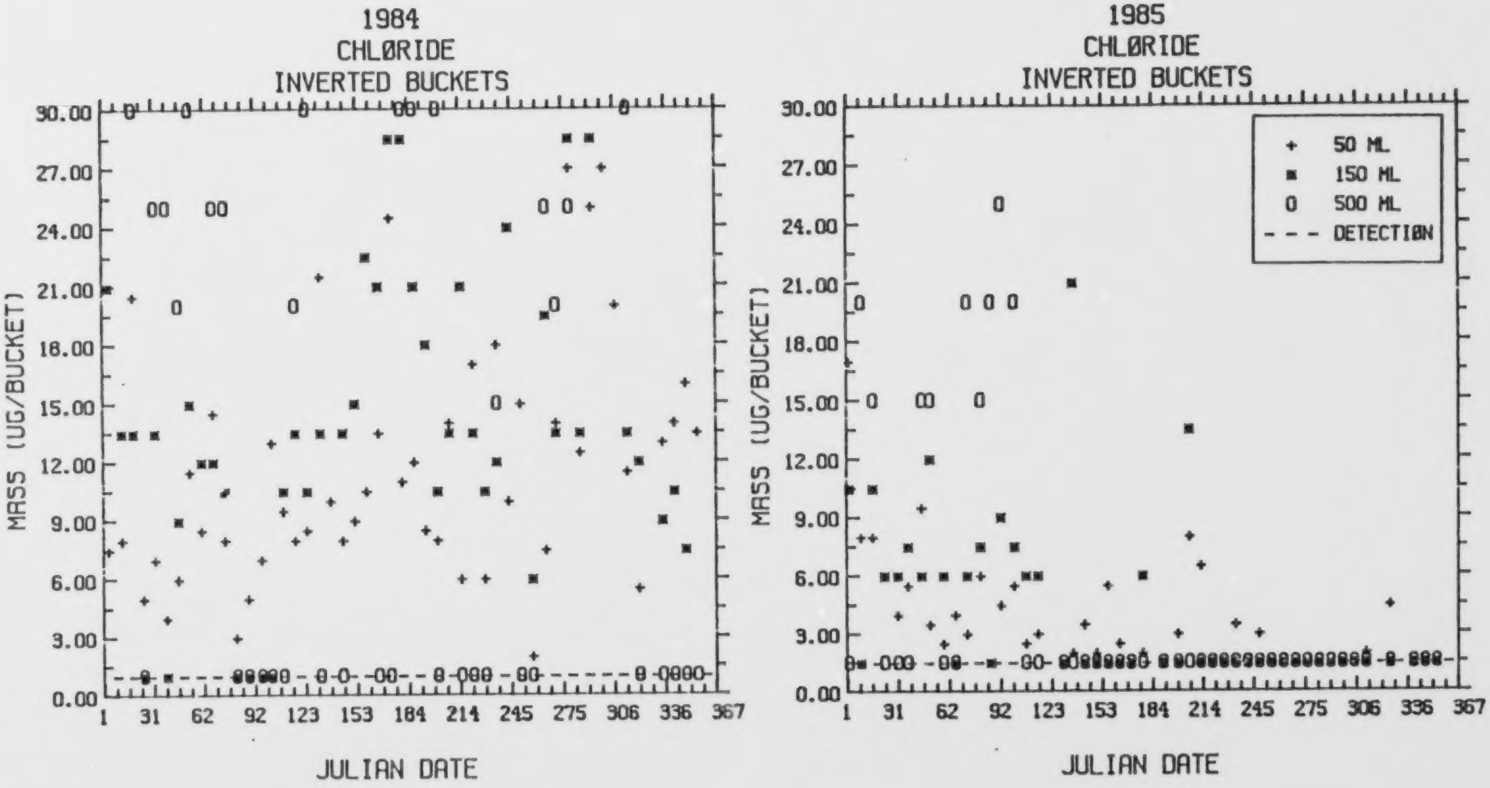


FIGURE 18. Measured chloride mass in inverted bucket blanks for 1984 and 1985.

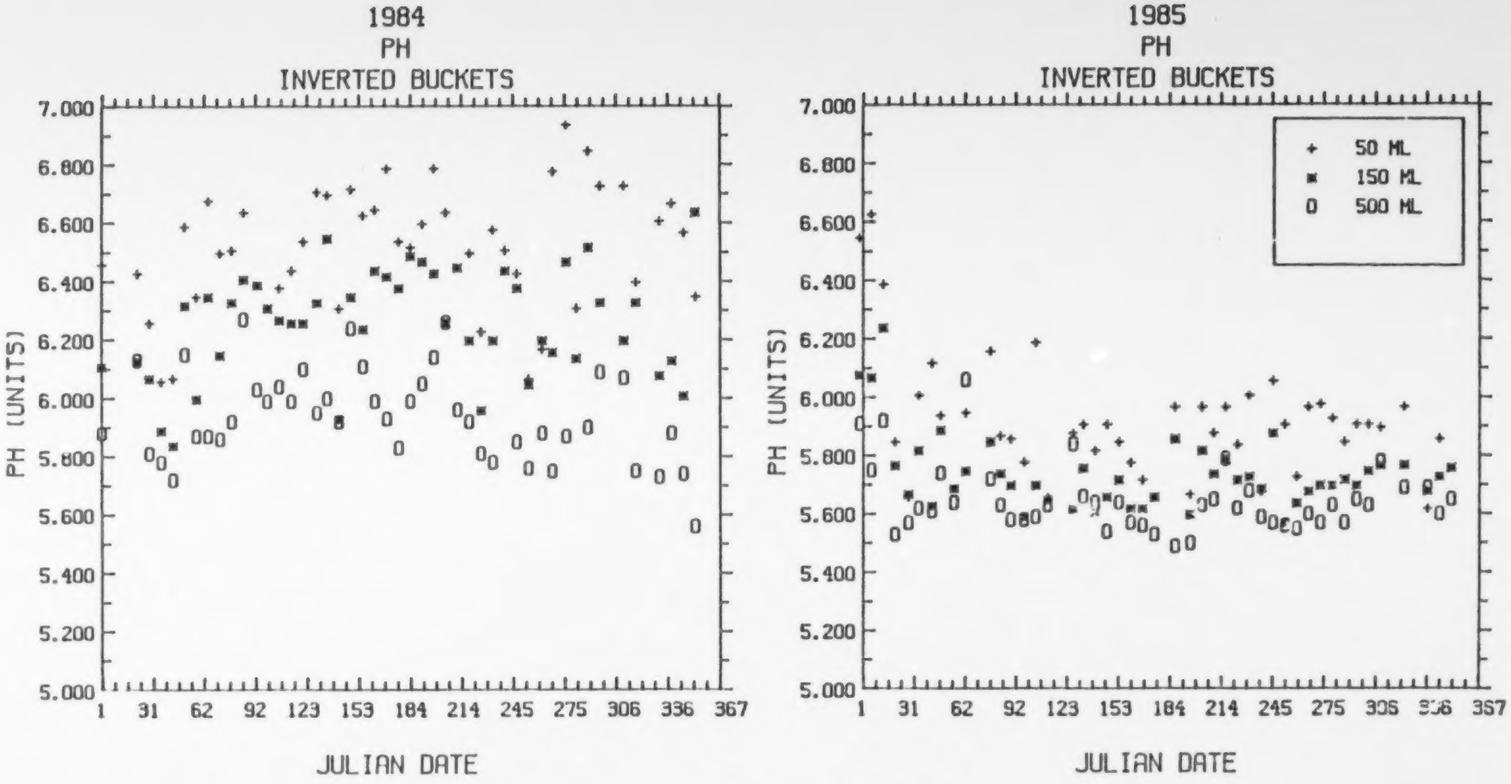


FIGURE 19. Measured pH in inverted bucket blanks for 1984 and 1985.

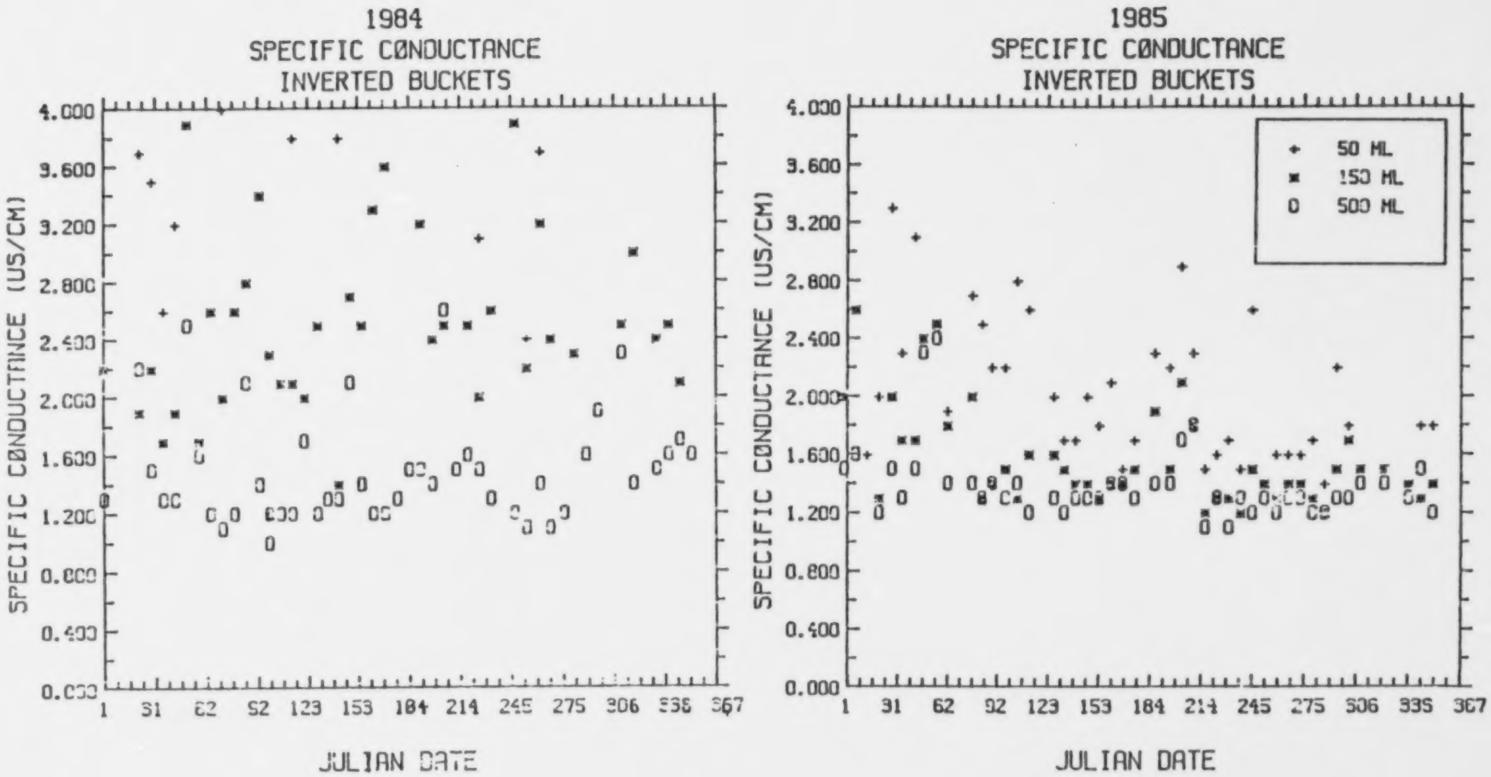


FIGURE 20. Measured specific conductance in inverted bucket blanks for 1984 and 1985.

TABLE 1 Minimum Detectable Mass Values for Bucket Blanks Analyzed in 1984 and 1985.

Analyte	**Minimum Mass Value (ug/bucket)** **1984**	 **1985**
Calcium	0.45	0.45
Magnesium	0.15	0.15
Sodium	0.15	0.15
Potassium	0.15	0.15
Ammonium	1.0	1.0
Sulfate	5.0	1.5
Nitrate-Nitrite	1.0	1.5
Chloride	1.0	1.5
Orthophosphate	0.15	0.15

TABLE 2 Analyte Concentration Summary for Filter Leachate A for 1984.

Analyte	n[a]	Detection Limit (mg/L)	Frequency of MDL (%)	Percentile (mg/L) 50th	95th
Calcium	50	0.009	98.0	<0.009	<0.009
Magnesium	50	0.003	90.0	<0.003	0.004
Sodium	50	0.003	46.0	0.004	0.012
Potassium	50	0.003	84.0	<0.003	0.004
Ammonium	50	0.02	78.0	<0.02	0.05
Sulfate	50	0.10	74.0	<0.10	0.39
Nitrate-Nitrite	50	0.02	88.0	<0.02	0.02
Chloride	50	0.02	78.0	<0.02	0.05
Ortho-phosphate	50	0.003	90.0	<0.003	0.010

a. number of analyses

TABLE 3 Analyte Concentration Summary for Filter Leachate B for 1984.

Analyte	n[a]	Detection Limit (mg/L)	Frequency of MDL (%)	Percentile (mg/L) 50th	95th
Calcium	50	0.009	96.0	<0.009	<0.009
Magnesium	50	0.003	94.0	<0.003	<0.003
Sodium	50	0.003	80.0	<0.003	0.006
Potassium	50	0.003	90.0	<0.003	0.004
Ammonium	50	0.02	80.0	<0.02	0.05
Sulfate	50	0.10	80.0	<0.10	0.41
Nitrate-Nitrite	50	0.02	100.0	<0.02	<0.02
Chloride	50	0.02	88.0	<0.02	<0.02
Ortho-phosphate	50	0.003	80.0	<0.003	0.007

a. number of analyses

TABLE 4 Analyte Concentration Summary for Filter Leachate A for 1985.

Analyte	n^a	Detection Limit (mg/L)	Frequency of MDL (%)	Percentile (mg/L)	
				50th	95th
Calcium	47	0.009	87.0	<0.009	0.010
Magnesium	47	0.003	59.6	<0.003	0.006
Sodium	47	0.003	23.4	0.010	0.042
Potassium	47	0.003	95.7	<0.003	<0.003
Ammonium	45	0.02	97.8	<0.02	<0.02
Sulfate					
AC	15	0.10	100.0	<0.10	<0.10
IC	30	0.03	86.7	<0.03	0.04
Nitrate-Nitrite AC	15	0.02	93.3	<0.02	0.02
Nitrate IC	30	0.03	90.0	<0.03	0.05
Chloride					
AC	15	0.02	66.7	<0.02	0.04
IC	30	0.03	70.0	<0.03	0.06
Ortho-phosphate	45	0.003	64.4	<0.003	0.023

a. number of analyses

TABLE 5 Analyte Concentration Summary for Filter Leachate B for 1985.

Analyte	n^a	Detection Limit (mg/L)	Frequency of MDL (%)	Percentile (mg/L)	
				50th	95th
Calcium	47	0.009	95.7	<0.009	<0.009
Magnesium	47	0.003	91.5	<0.003	0.003
Sodium	47	0.003	72.3	<0.003	0.007
Potassium	47	0.003	97.9	<0.003	<0.003
Ammonium	45	0.02	100.0	<0.02	<0.02
Sulfate					
AC	15	0.10	80.0	<0.10	0.35
Nitrate-Nitrite AC	15	0.02	93.3	<0.02	0.02
Nitrate IC	30	0.03	96.7	<0.03	<0.03
Chloride					
AC	15	0.02	93.3	<0.02	0.02
IC	30	0.03	100.0	<0.03	<0.03
Ortho-phosphate	45	0.003	82.2	<0.003	0.010

a. number of analyses

TABLE 6 Median pH and Specific Conductance Measurements Found in Filter Leachates A and B for 1984 and 1985.

Leachate Analyte	Median Value Measured A 1984	 1985	 B 1984	 1985
pH (units)	5.60	5.56	5.59	5.56
Specific Conductance (uS/cm)	1.2	1.3	1.2	1.5
n[a]	50	47	50	47

a. number of analyses

TABLE 7 Median Analyte Concentration Values for Deionized Water Blank for 1984-1985.

	Median Concentration Value (mg/L)			
	Room 61[a]		Room 129[a]	
Analyte	1984	1985	1984	1985
pH (units)	5.59	5.57	5.60	5.61
Specific Conductance (uS/cm)	1.1	1.0	1.1	1.0
n[b]	49	41	32	37

a. sample processing laboratory is room 61 and atomic absorption spectroscopy laboratory is room 129
b. number of analyses

TABLE 8 Analyte Concentration Summary for the Sample Processing Laboratory Deionized Water for 1984.

Analyte	n[a]	Detection Limit (mg/L)	Frequency of MDL (%)	Percentile (mg/L) 50th	95th
Calcium	48	0.009	100.0	<0.009	<0.009
Magnesium	48	0.003	97.9	<0.003	<0.003
Sodium	48	0.003	91.7	<0.003	0.003
Potassium	48	0.003	100.0	<0.003	<0.003
Ammonium	49	0.02	91.8	<0.02	0.03
Sulfate	49	0.10	73.5	<0.10	0.35
Nitrate-Nitrite	49	0.02	100.0	<0.02	<0.02
Chloride	49	0.02	100.0	<0.02	<0.02
Ortho-phosphate	49	0.003	95.9	<0.003	<0.003

a. number of analyses

TABLE 9 Analyte Concentration Summary for the Sample Processing Laboratory Deionized Water for 1985.

Analyte	n[a]	Detection Limit (mg/L)	Frequency of MDL (%)	Percentile (mg/L) 50th	95th
Calcium	41	0.009	100.0	<0.009	<0.009
Magnesium	41	0.003	100.0	<0.003	<0.003
Sodium	41	0.003	92.7	<0.003	0.003
Potassium	41	0.003	97.6	<0.003	<0.003
Ammonium	41	0.02	97.6	<0.02	<0.02
Sulfate					
AC	17	0.10	88.2	<0.10	0.12
IC	24	0.03	87.5	<0.03	0.03
Nitrate-					
Nitrite AC	17	0.02	94.1	<0.02	0.02
Nitrate IC	24	0.03	95.8	<0.03	<0.03
Chloride					
AC	17	0.02	100.0	<0.02	<0.02
IC	24	0.03	95.8	<0.03	<0.03
Ortho-phosphate	41	0.003	85.4	<0.003	0.006

a. number of analyses

TABLE 10 Analyte Concentration Summary for the Atomic Absorption Spectroscopy Laboratory Deionized Water for 1984.

Analyte	n[a]	Detection Limit (mg/L)	Frequency of MDL (%)	Percentile (mg/L)	
				50th	95th
Calcium	29	0.009	100.0	<0.009	<0.009
Magnesium	29	0.003	96.6	<0.003	<0.003
Sodium	29	0.003	100.0	<0.003	<0.003
Potassium	29	0.003	96.6	<0.003	<0.003
Ammonium	32	0.02	90.6	<0.02	0.04
Sulfate	32	0.10	84.4	<0.10	0.37
Nitrate-Nitrite	32	0.02	100.0	<0.02	<0.02
Chloride	32	0.02	96.9	<0.02	<0.02
Ortho-phosphate	32	0.003	96.9	<0.003	<0.003

a. number of analyses

TABLE 11 Analyte Concentration Summary for the Atomic Absorption Spectroscopy Laboratory Deionized Water for 1985.

Analyte	n[a]	Detection Limit (mg/L)	Frequency of MDL (%)	Percentile (mg/L)	
				50th	95th
Calcium	37	0.009	100.0	<0.009	<0.009
Magnesium	37	0.003	94.6	<0.003	0.003
Sodium	37	0.003	94.6	<0.003	0.003
Potassium	37	0.003	100.0	<0.003	<0.003
Ammonium	37	0.02	100.0	<0.02	<0.02
Sulfate					
AC	13	0.10	84.6	<0.10	0.10
IC	24	0.03	91.7	<0.03	0.03
Nitrate-Nitrite AC	13	0.02	100.0	<0.02	<0.02
Nitrate IC	24	0.03	100.0	<0.03	<0.03
Chloride					
AC	13	0.02	100.0	<0.02	<0.02
IC	24	0.03	100.0	<0.03	<0.03
Ortho-phosphate	37	0.003	83.8	<0.003	0.010

a. number of analyses

APPENDIX C

Replicate Sample Analyses
Plots and Tables
1984-1985

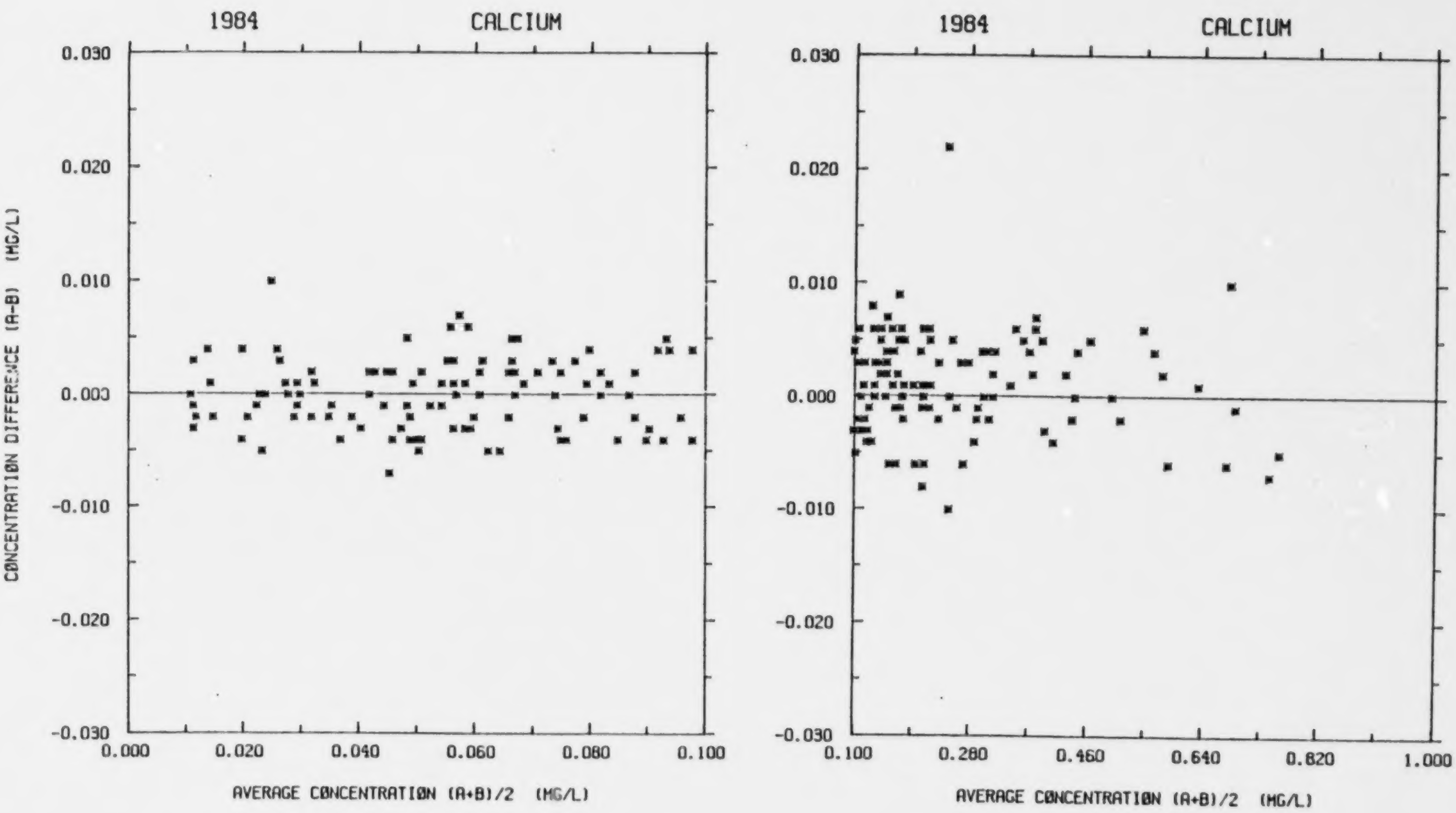


FIGURE 1. A/B replicate plots for calcium for 1984.

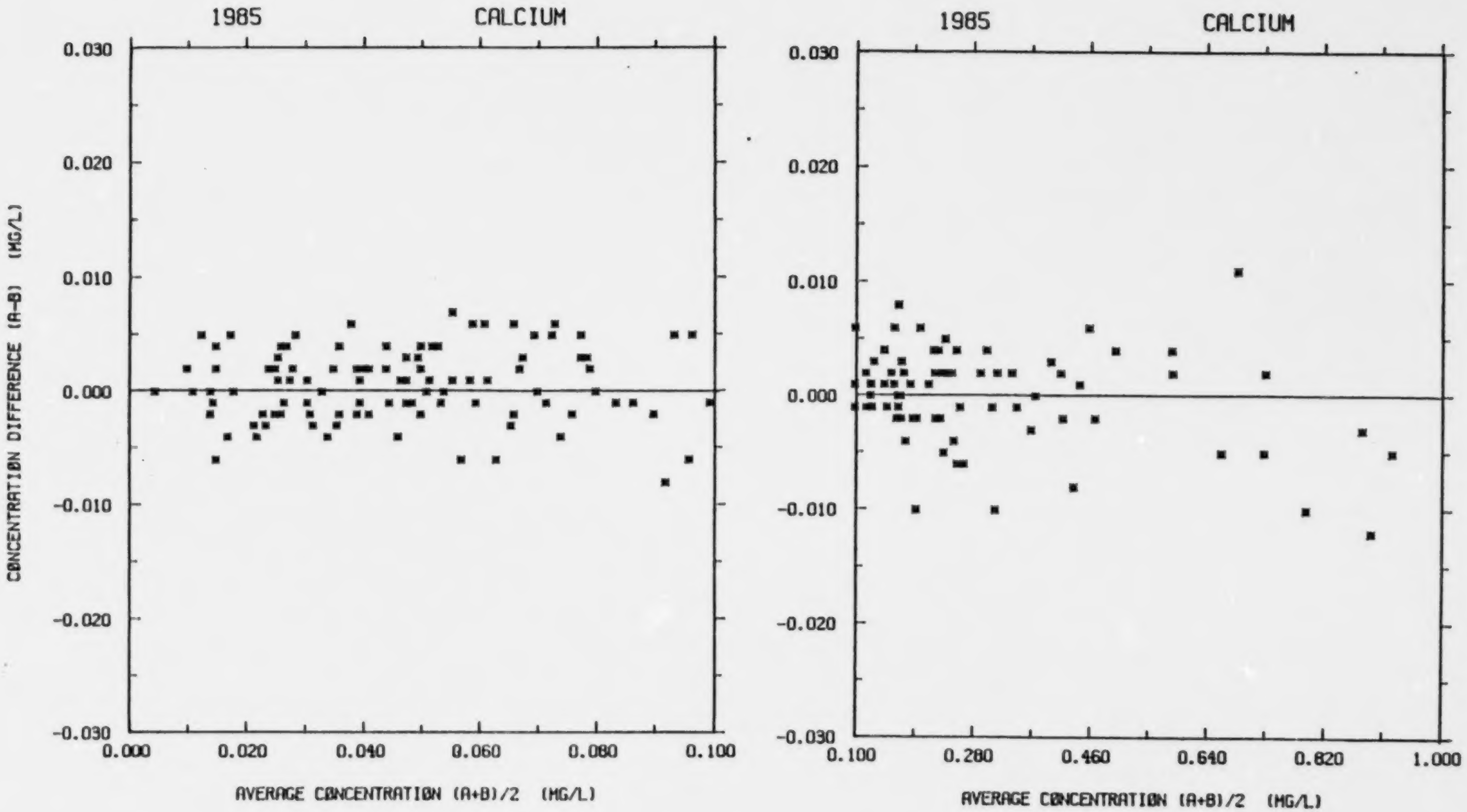


FIGURE 2. A/B replicate plots for calcium for 1985.

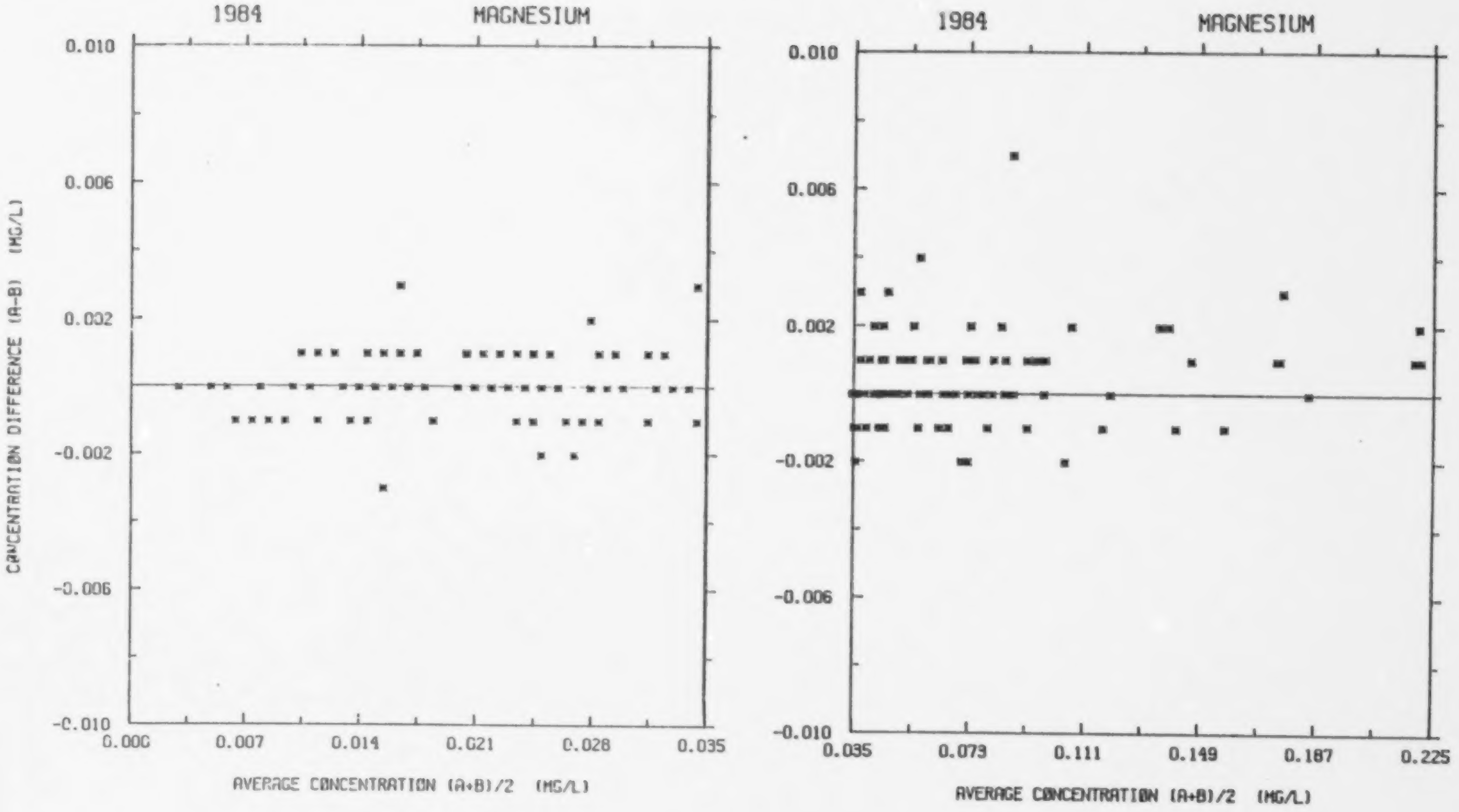


FIGURE 3. A/B replicate plots for magnesium for 1984.

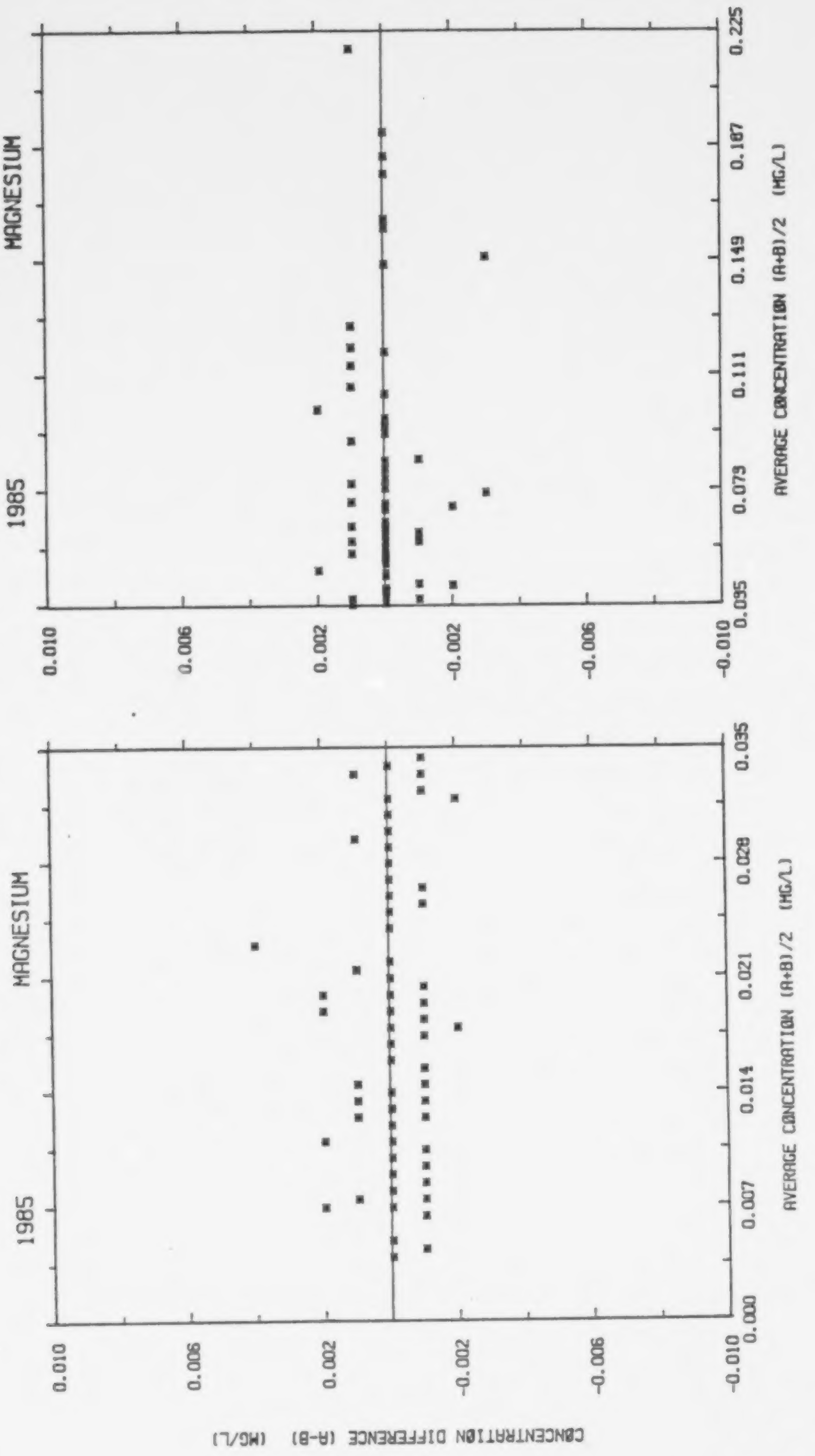


FIGURE 4. A/B replicate plots for magnesium for 1985.

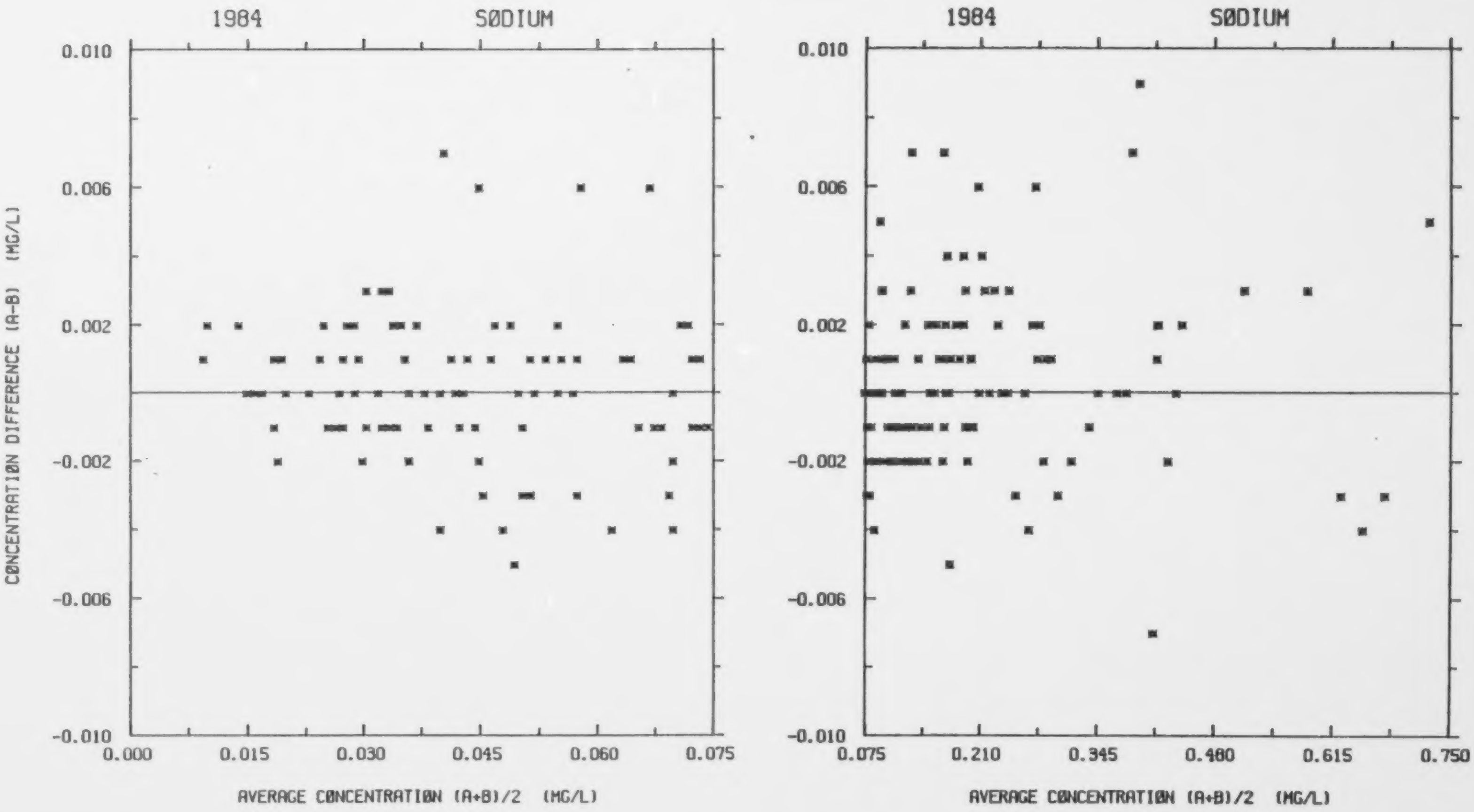


FIGURE 5. A/B replicate plots for sodium for 1984.

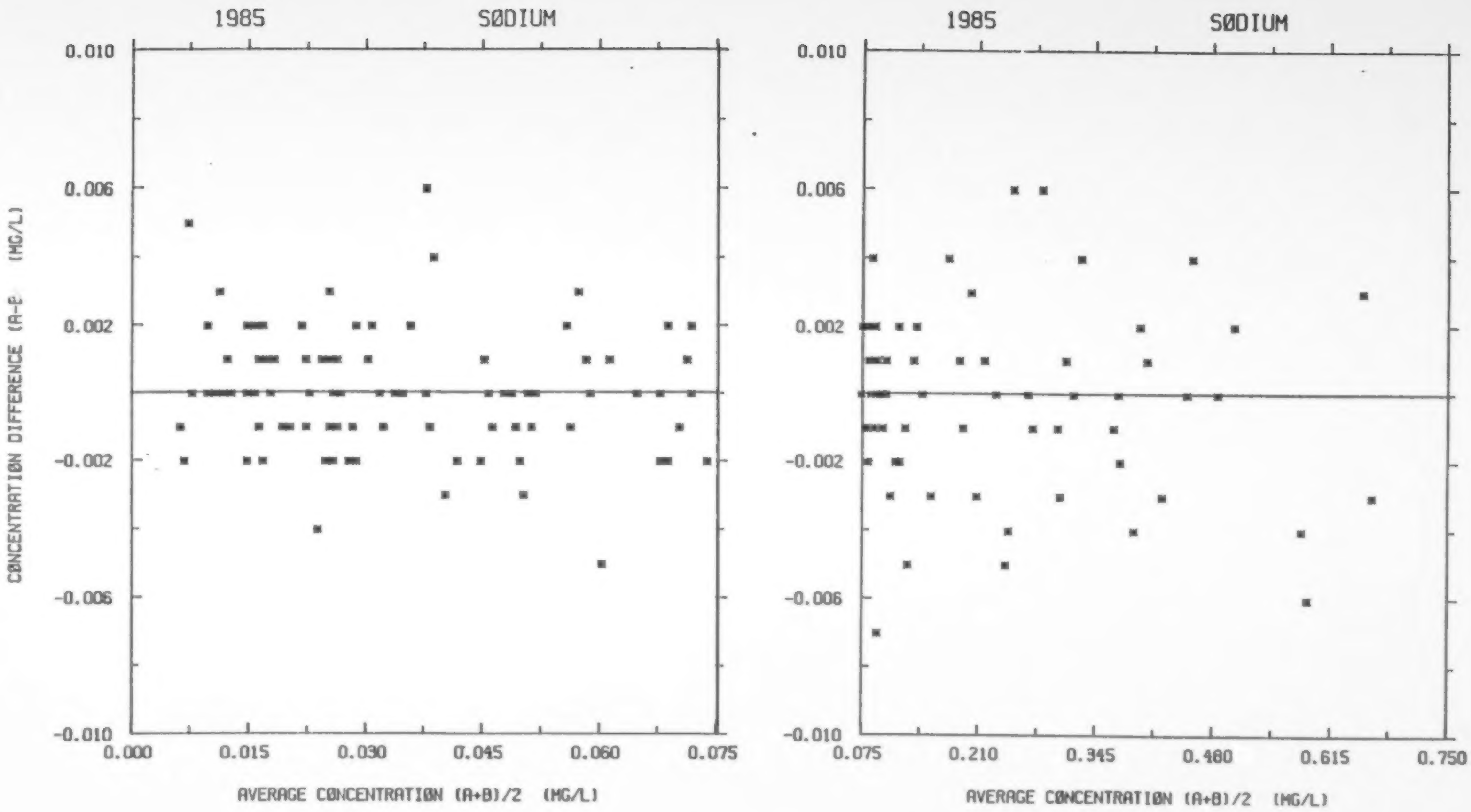


FIGURE 6. A/B replicate plots for sodium for 1985.

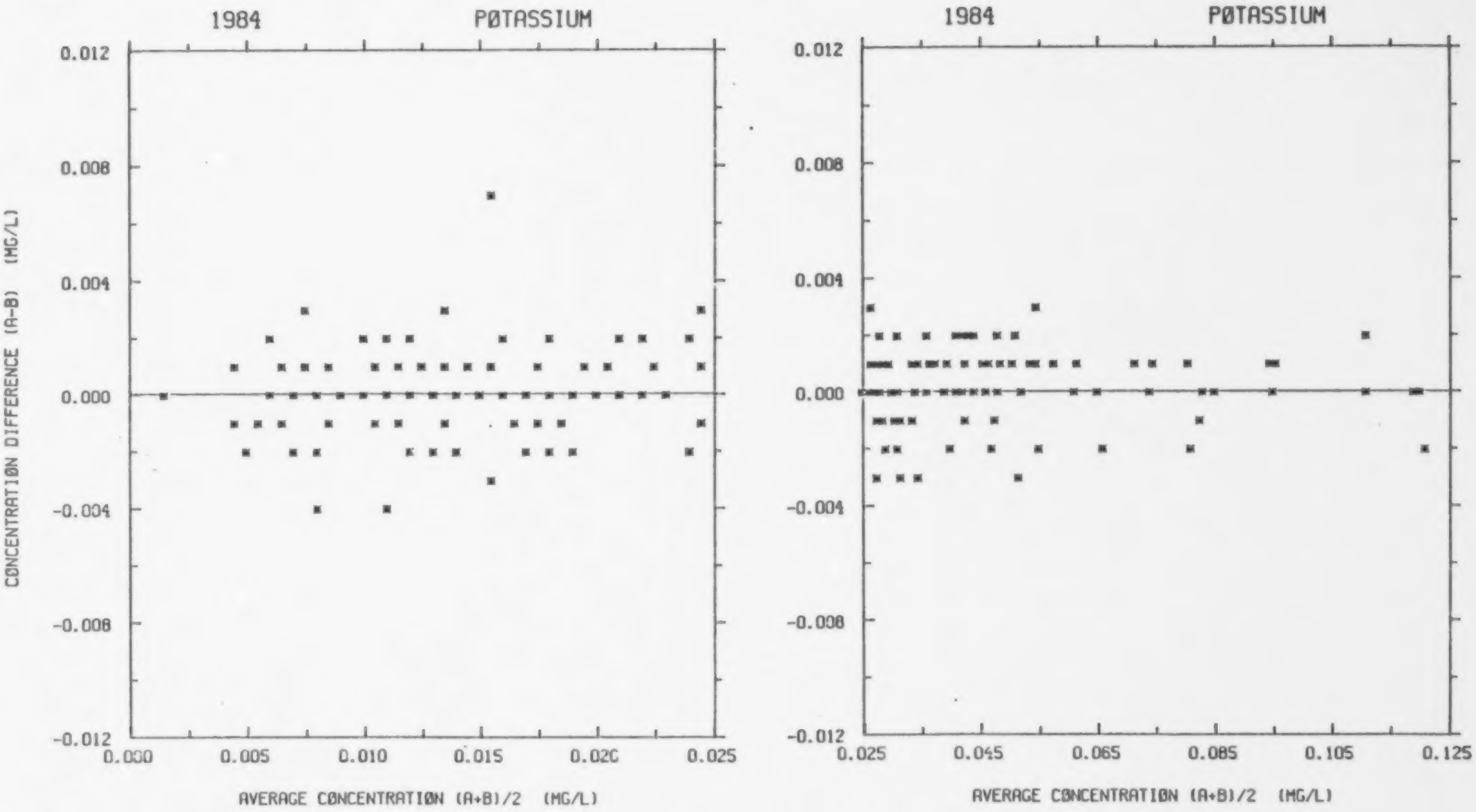


FIGURE 7. A/B replicate plots for potassium for 1984.

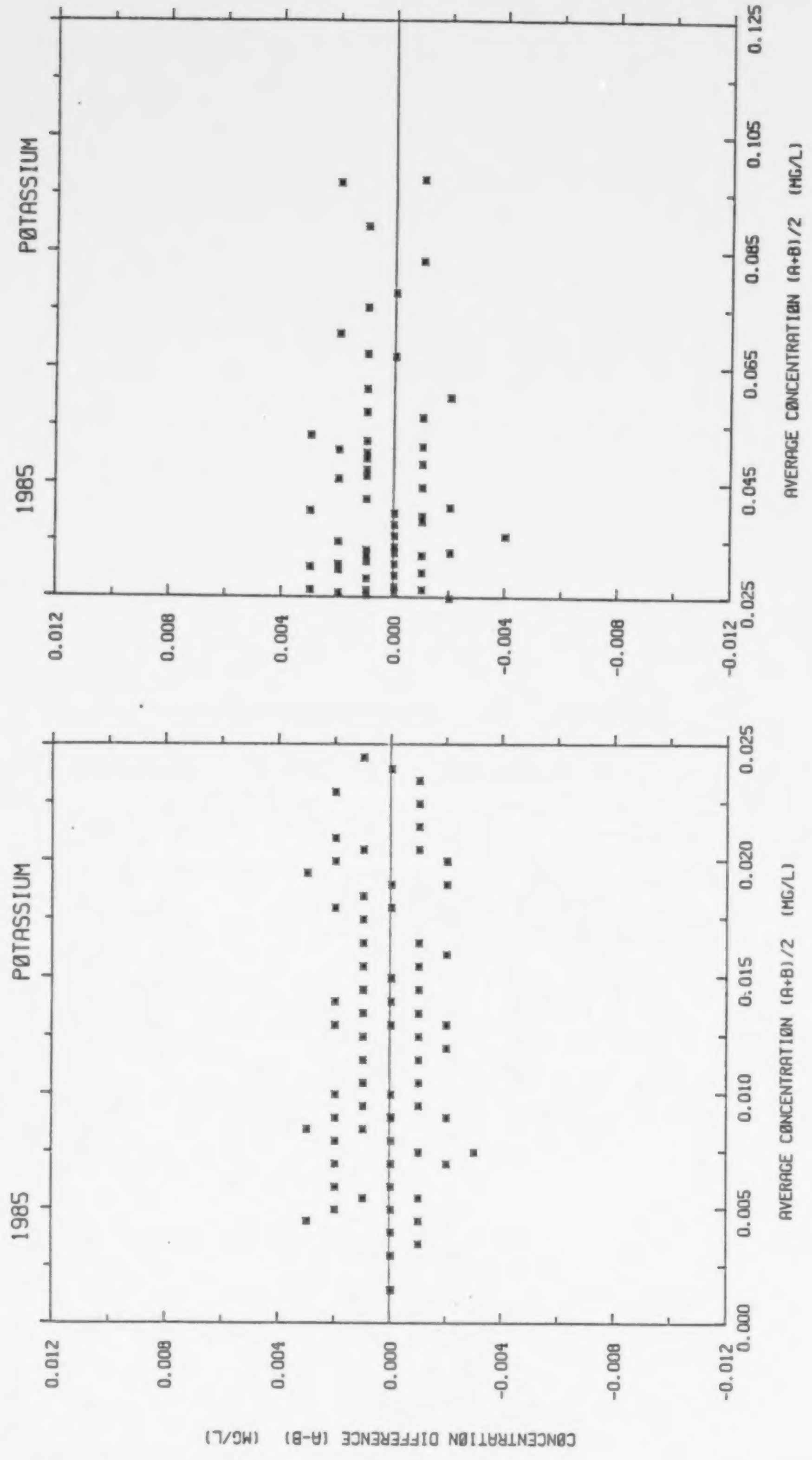


FIGURE 8. A/B replicate plots for potassium for 1985.

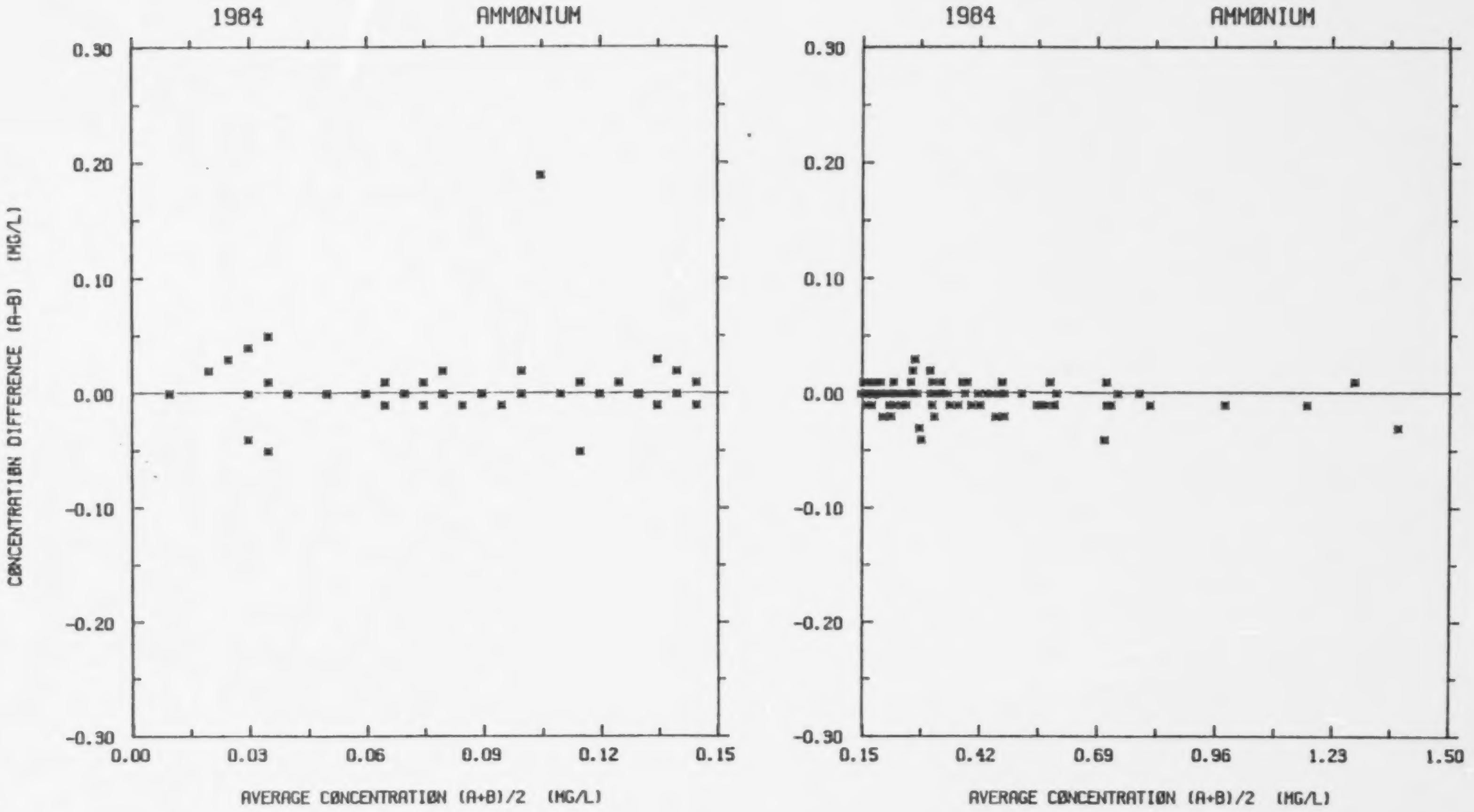


FIGURE 9. A/B replicate plots for ammonium for 1984.

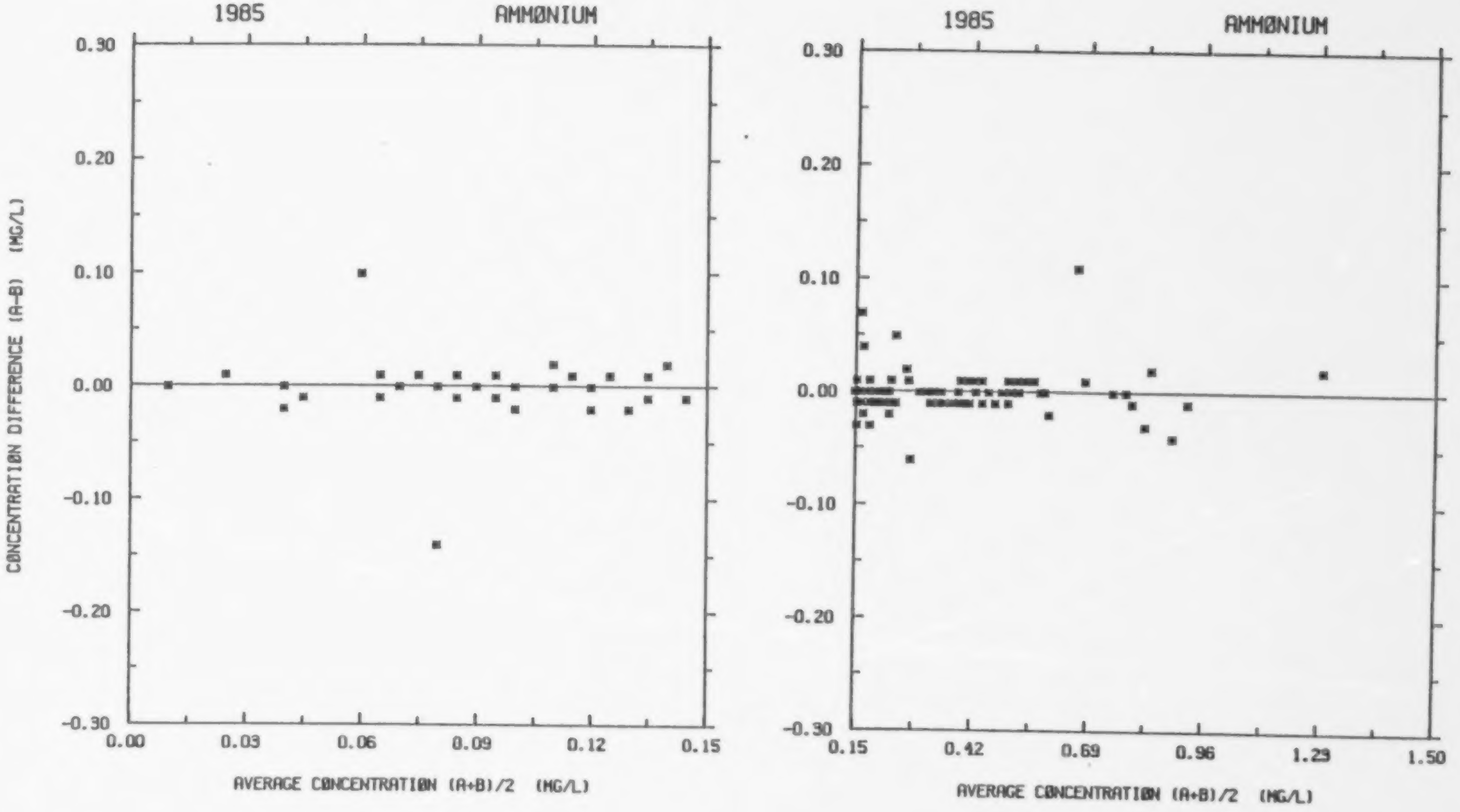


FIGURE 10. A/B replicate plots for ammonium for 1985.

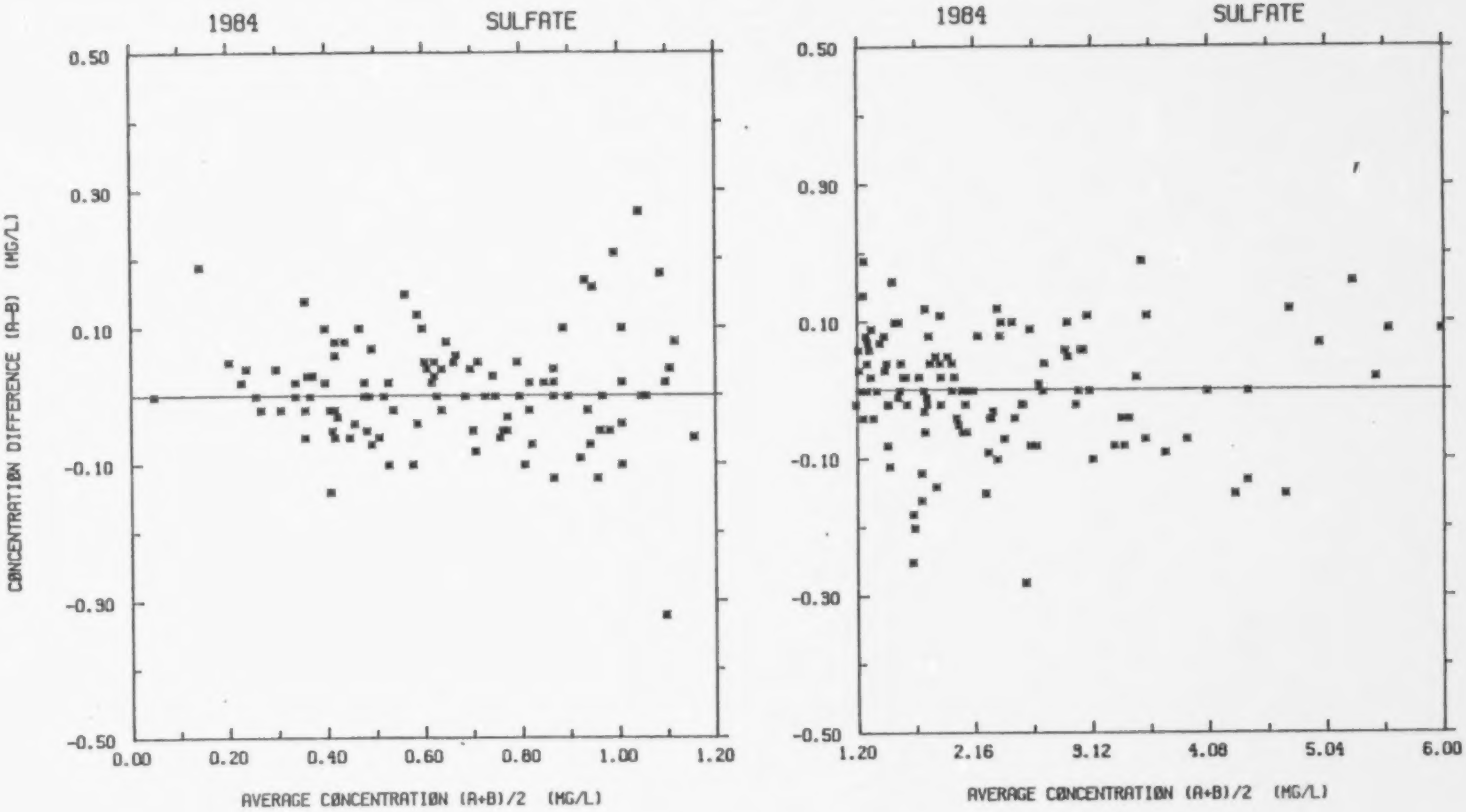


FIGURE 11. A/B replicate plots for sulfate for 1984.

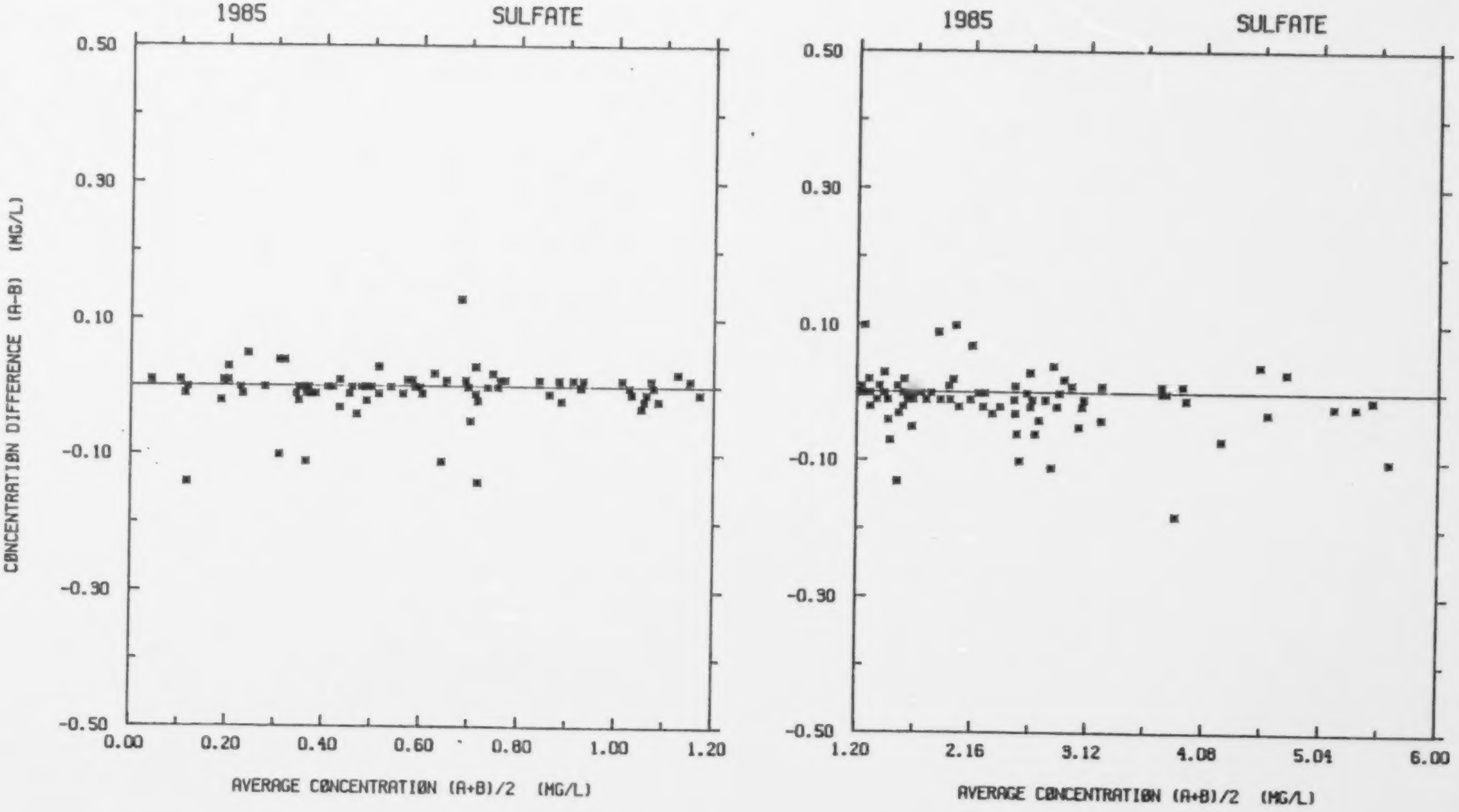


FIGURE 12. A/B replicate plots for sulfate for 1985.

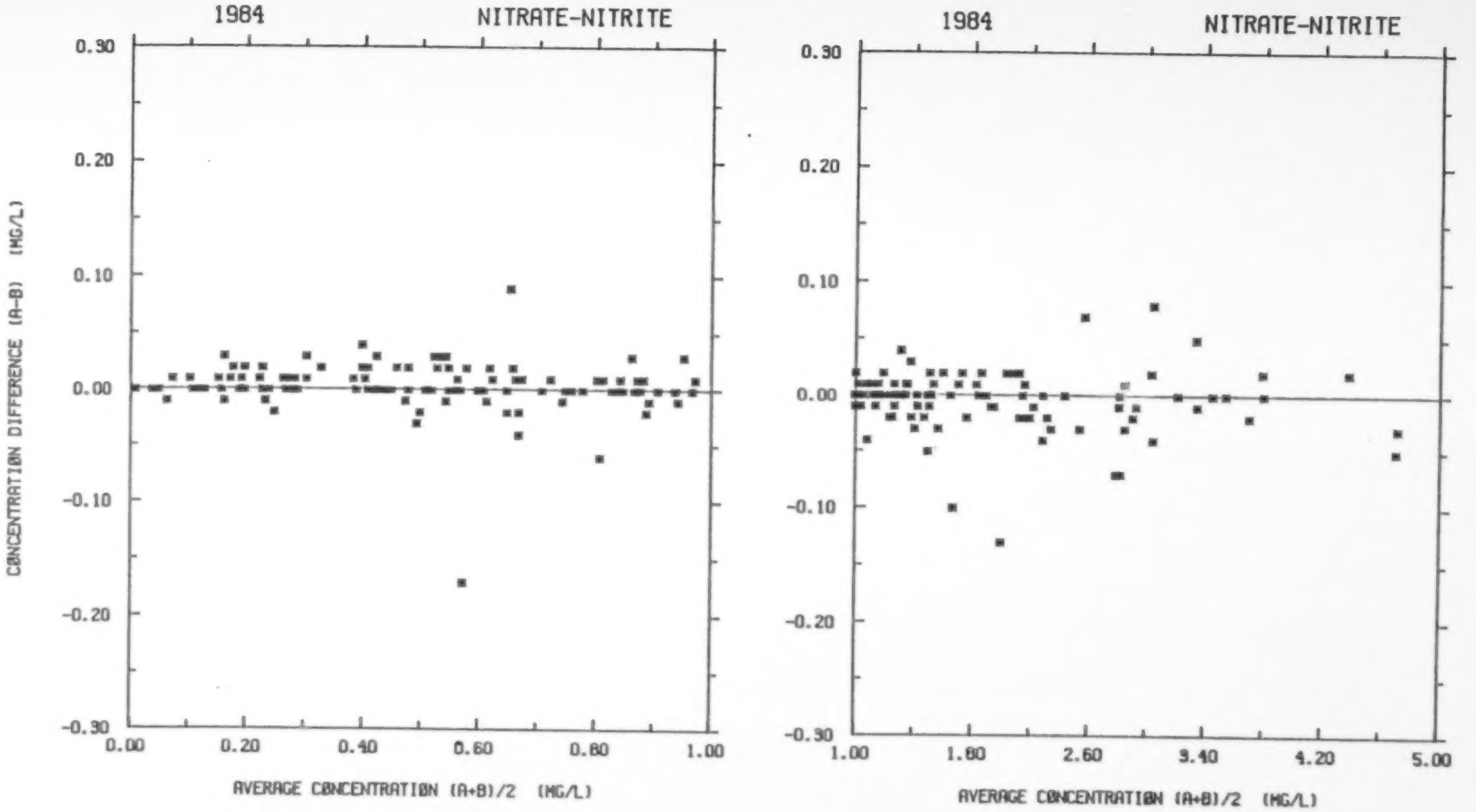


FIGURE 13. A/B replicate plots for nitrate-nitrite for 1984.

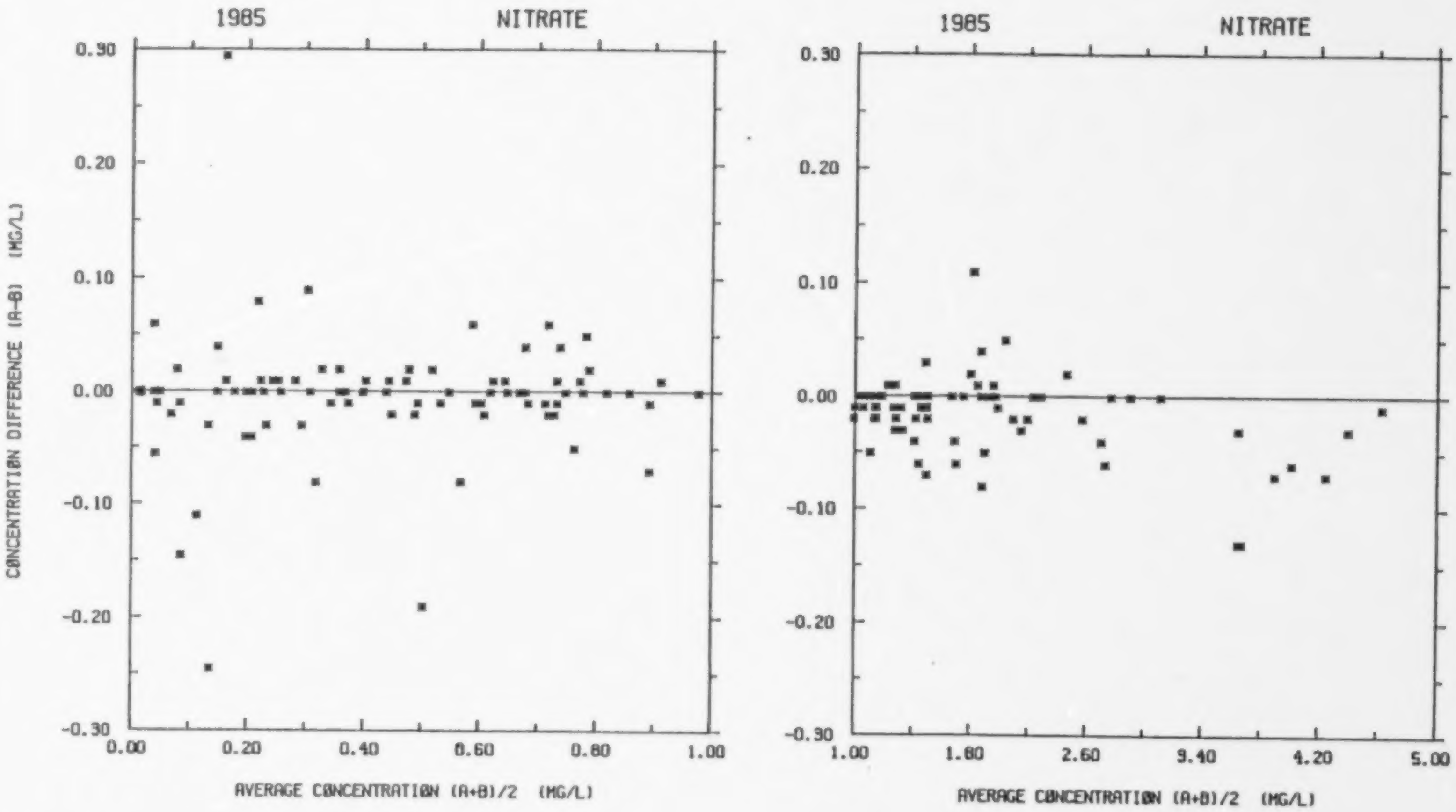


FIGURE 14. A/B replicate plots for nitrate for 1985.

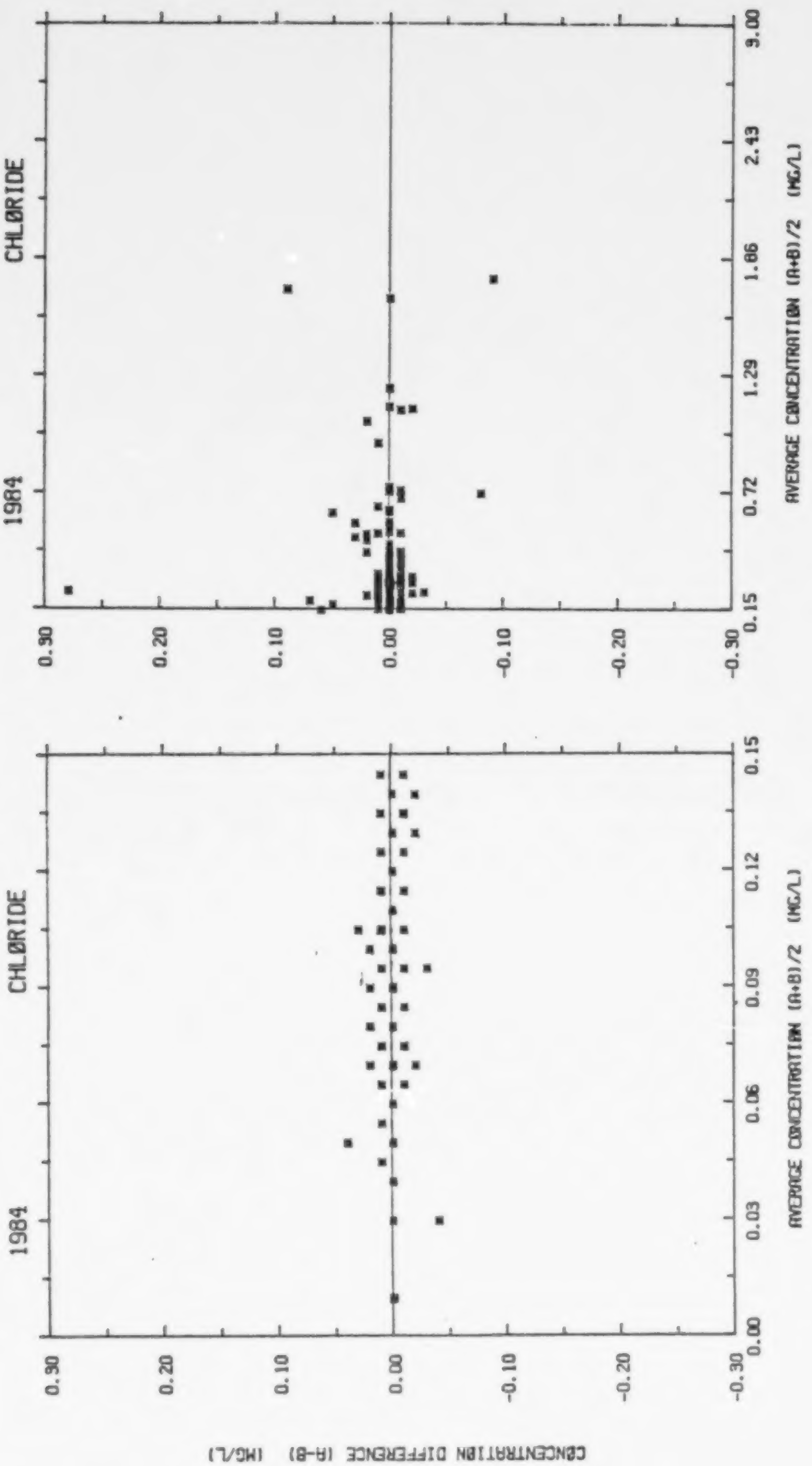


FIGURE 15. A/B replicate plots for chloride for 1984.

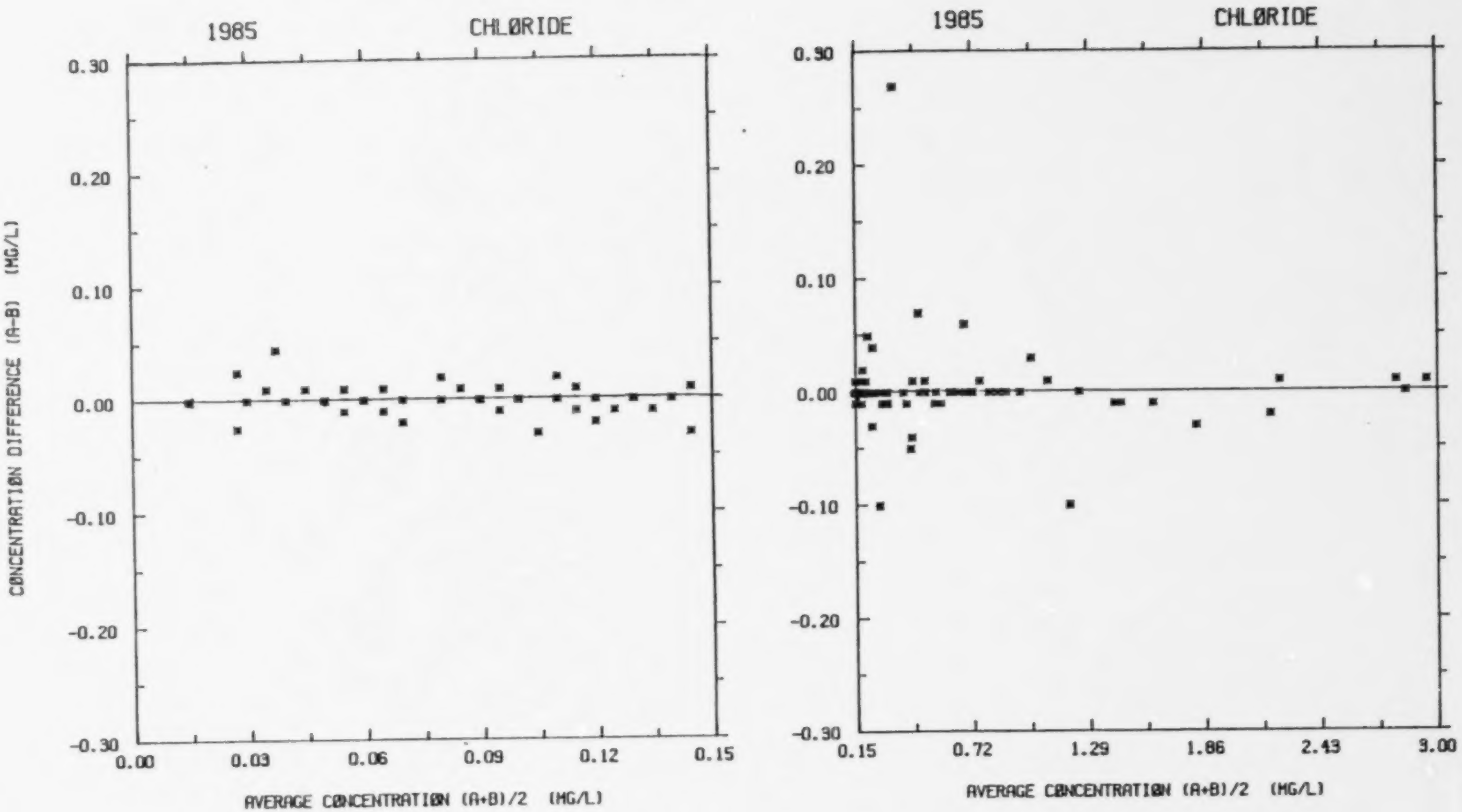


FIGURE 16. A/B replicate plots for chloride for 1985.

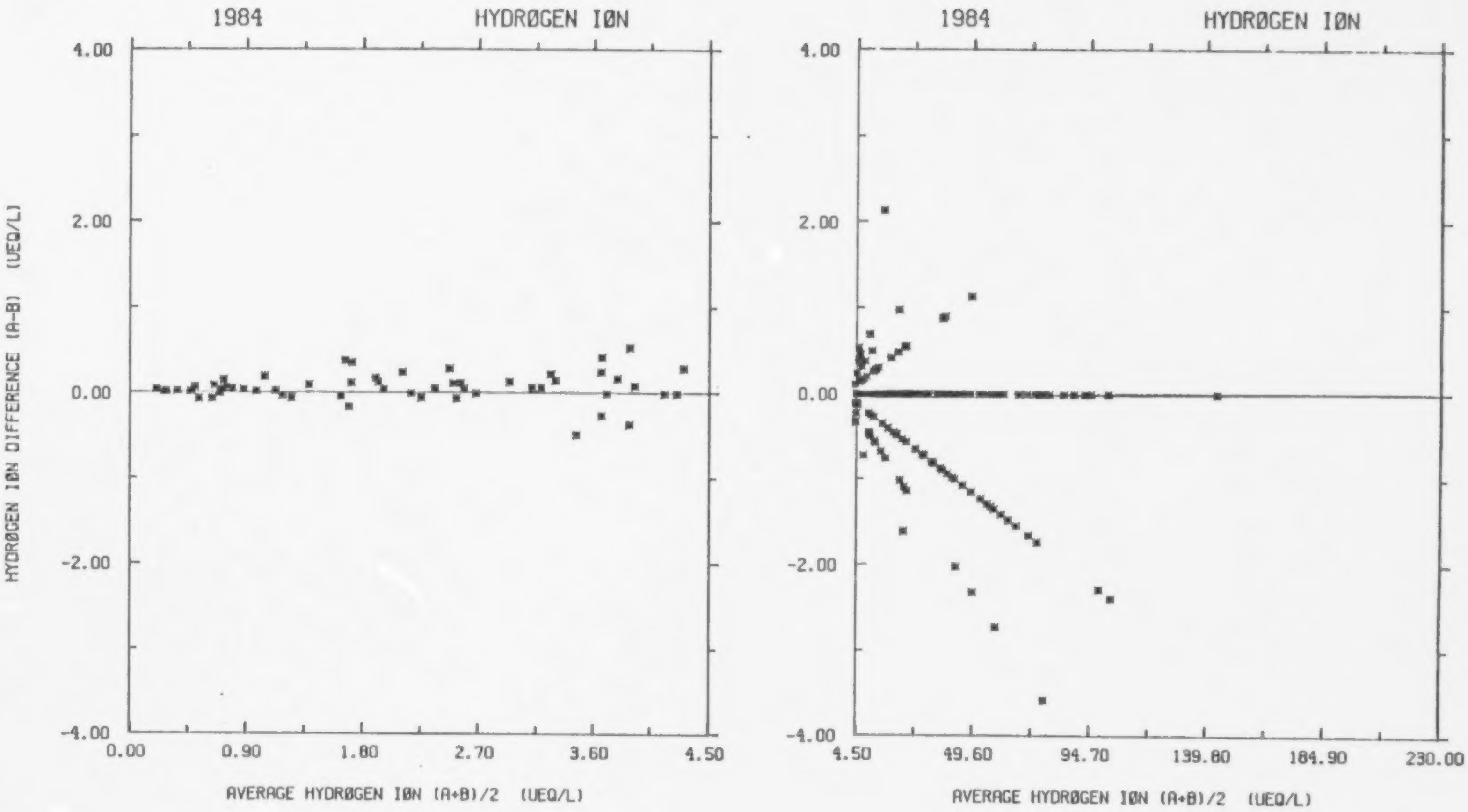


FIGURE 17. A/B replicate plots for hydrogen ion for 1984.

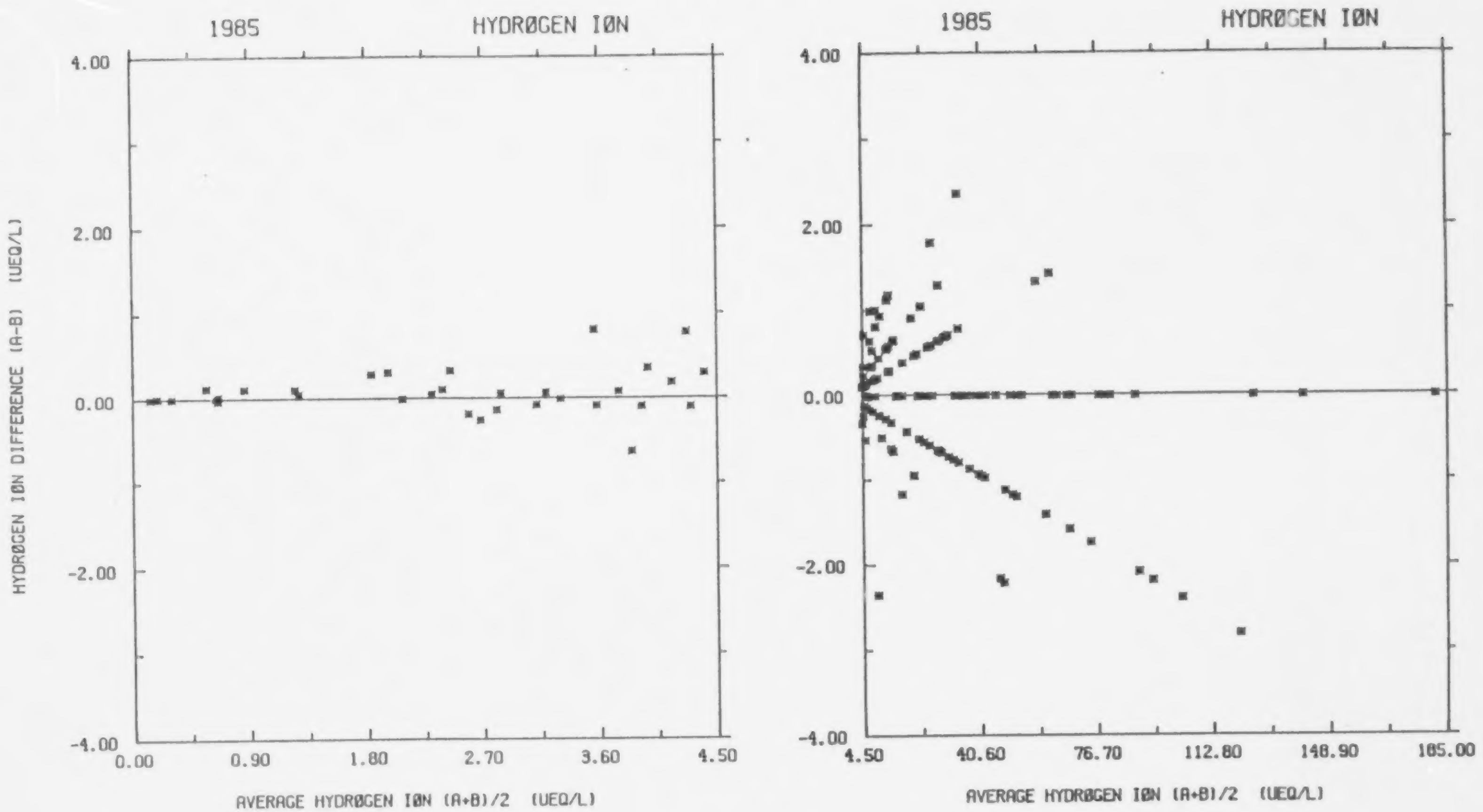


FIGURE 18. A/B replicate plots for hydrogen ion for 1985.

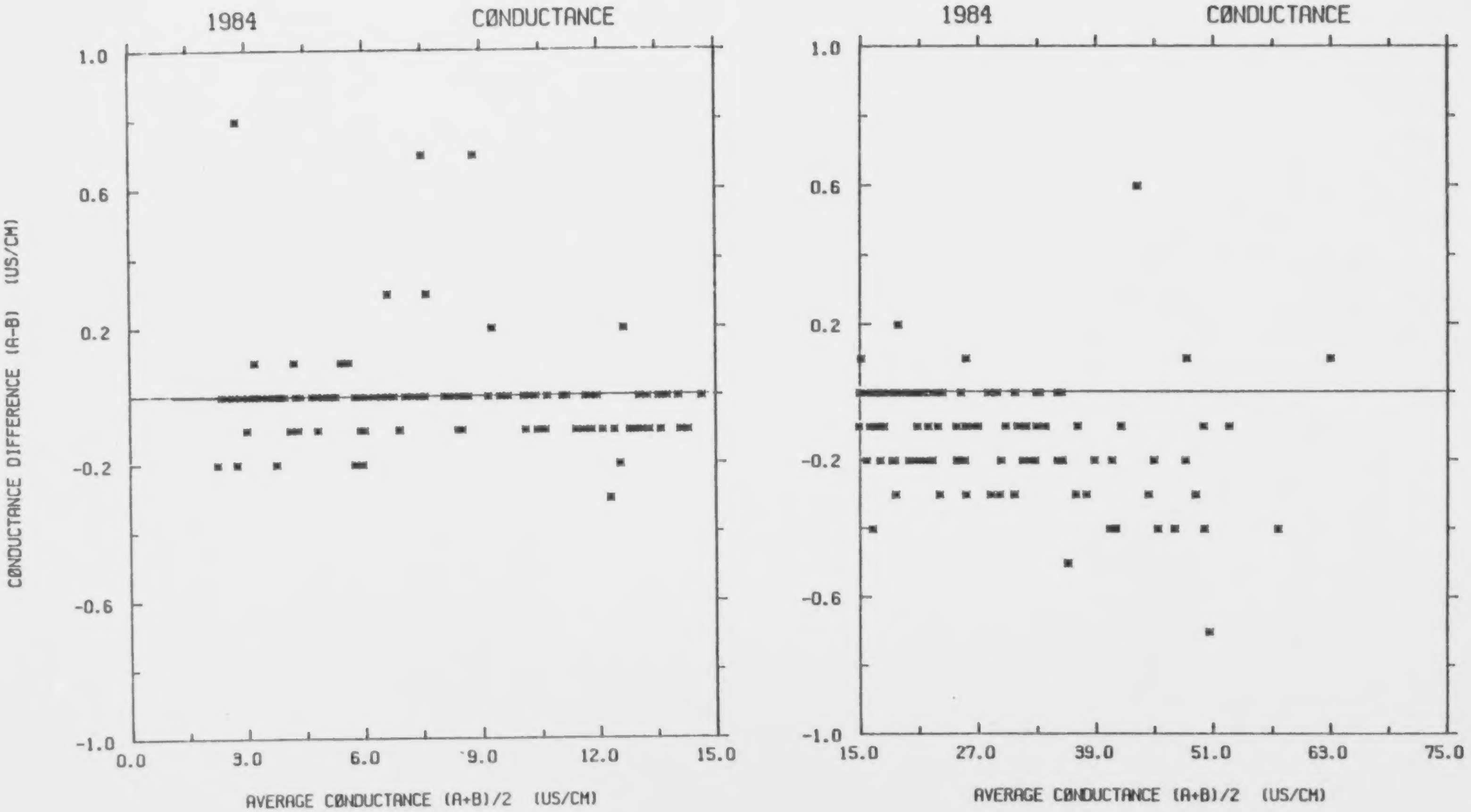


FIGURE 19. A/B replicate plots for specific conductance for 1984.

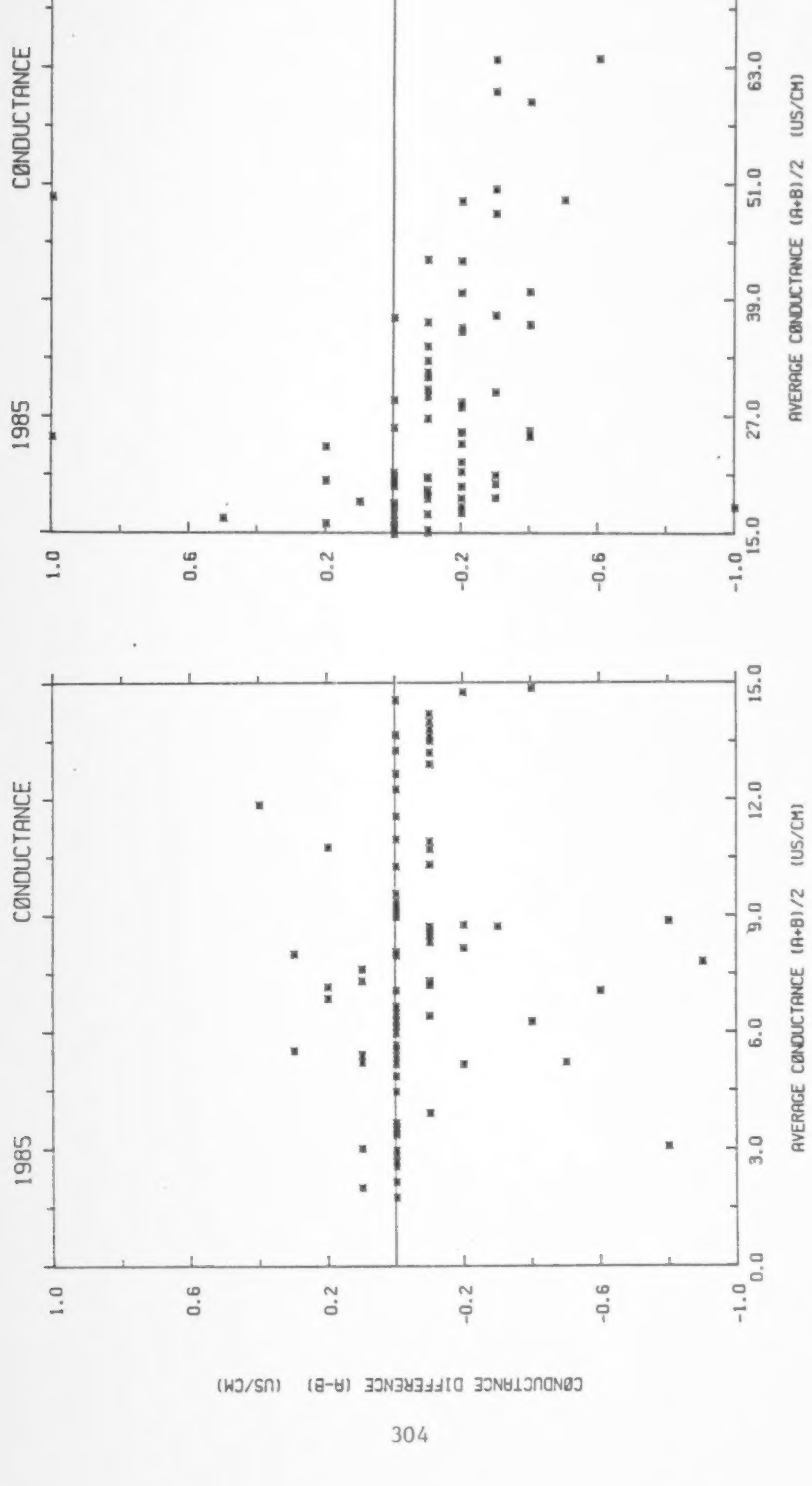


FIGURE 20. A/B replicate plots for specific conductance for 1985.

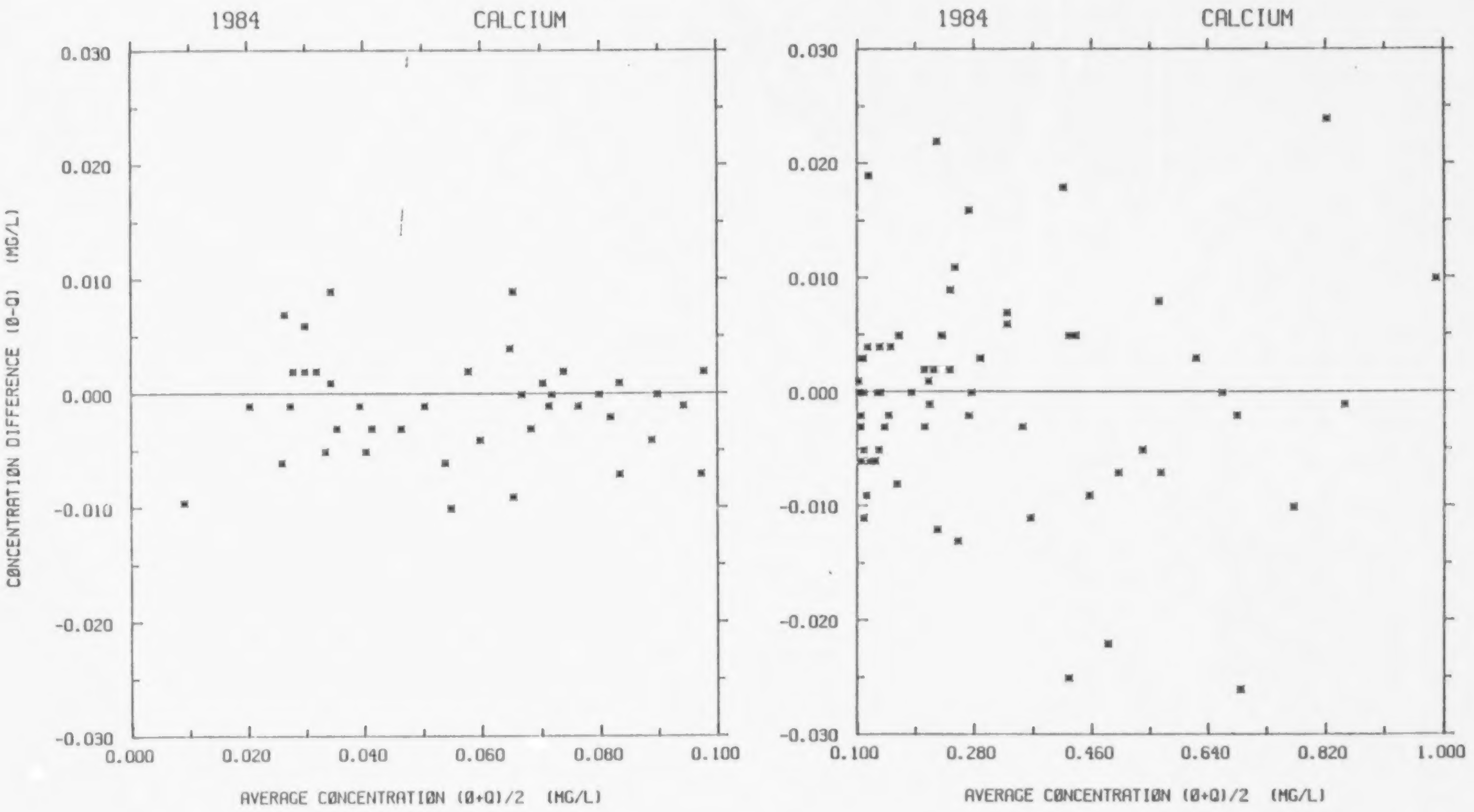


FIGURE 21. O/Q replicate plots for calcium for 1984.

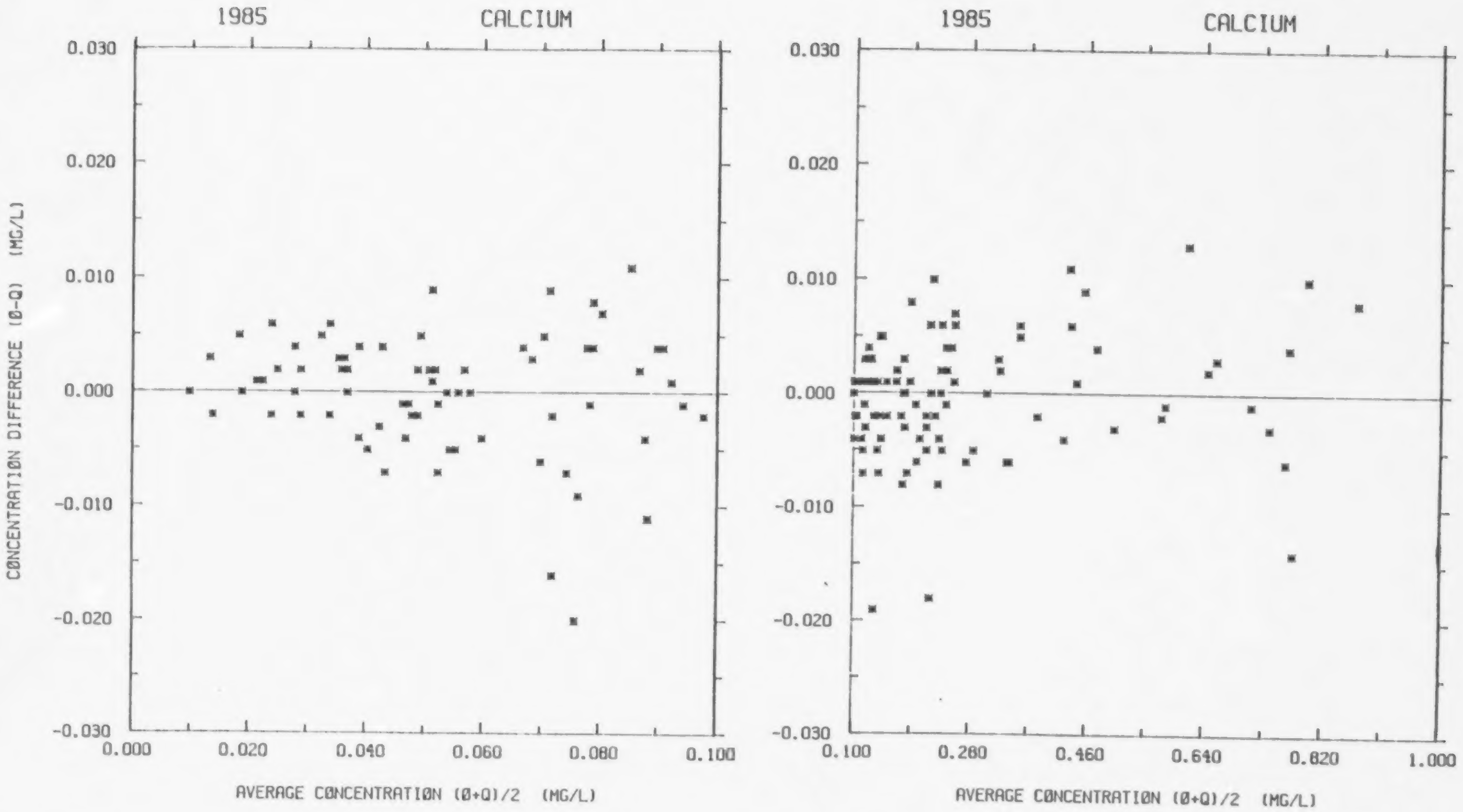


FIGURE 22. O/Q replicate plots for calcium for 1985.

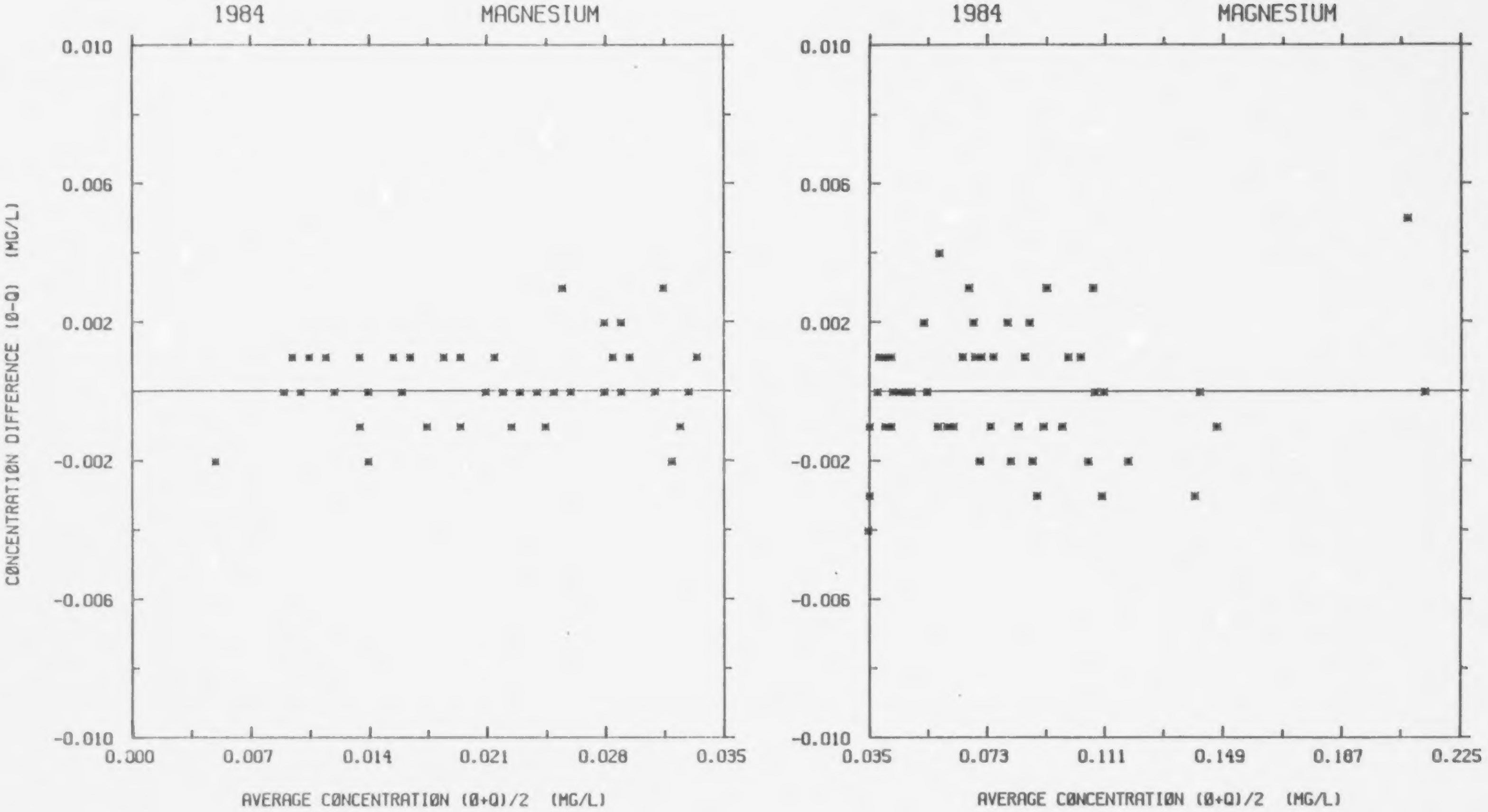


FIGURE 23. O/Q replicate plots for magnesium for 1984.

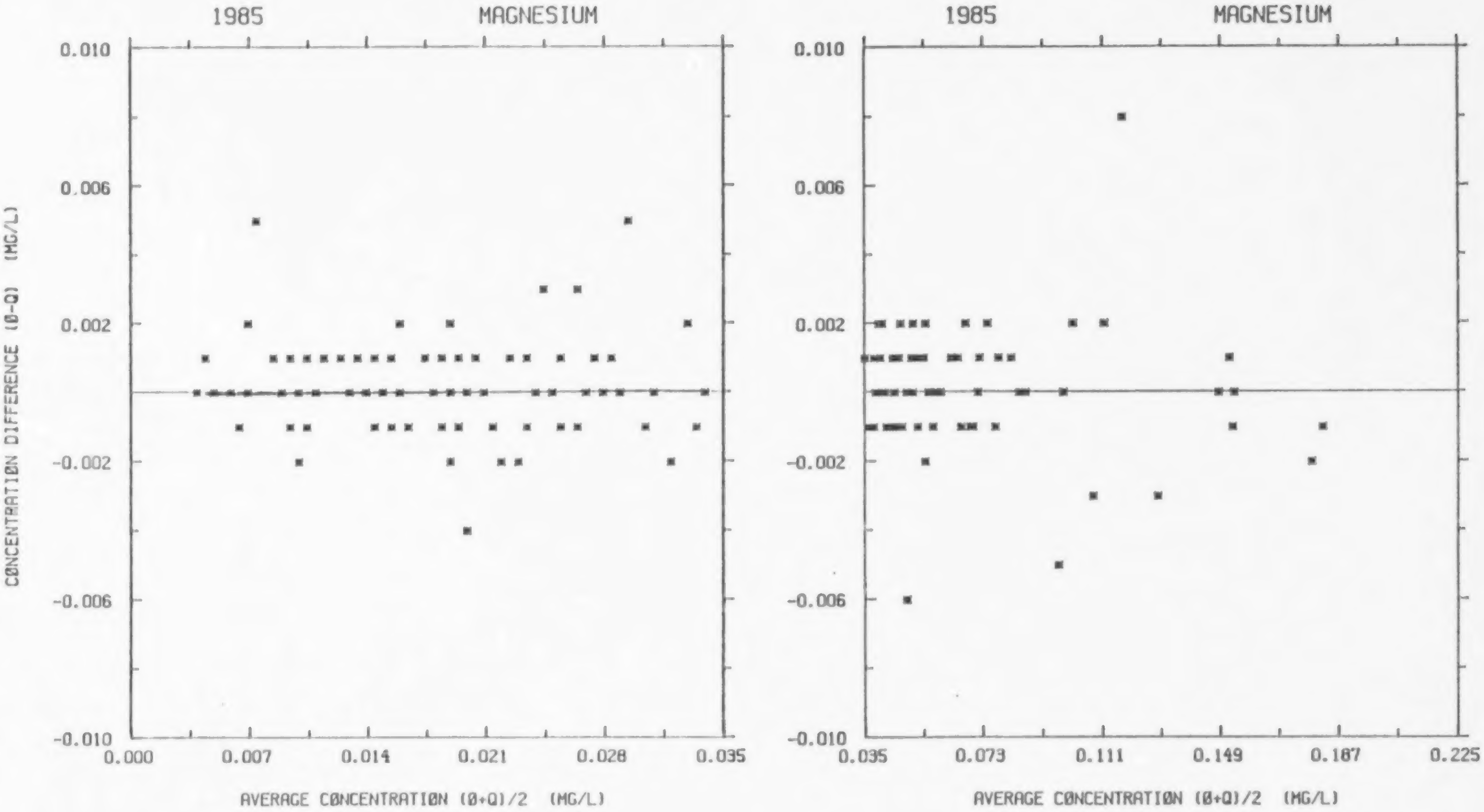


FIGURE 24. O/Q replicate plots for magnesium for 1985.

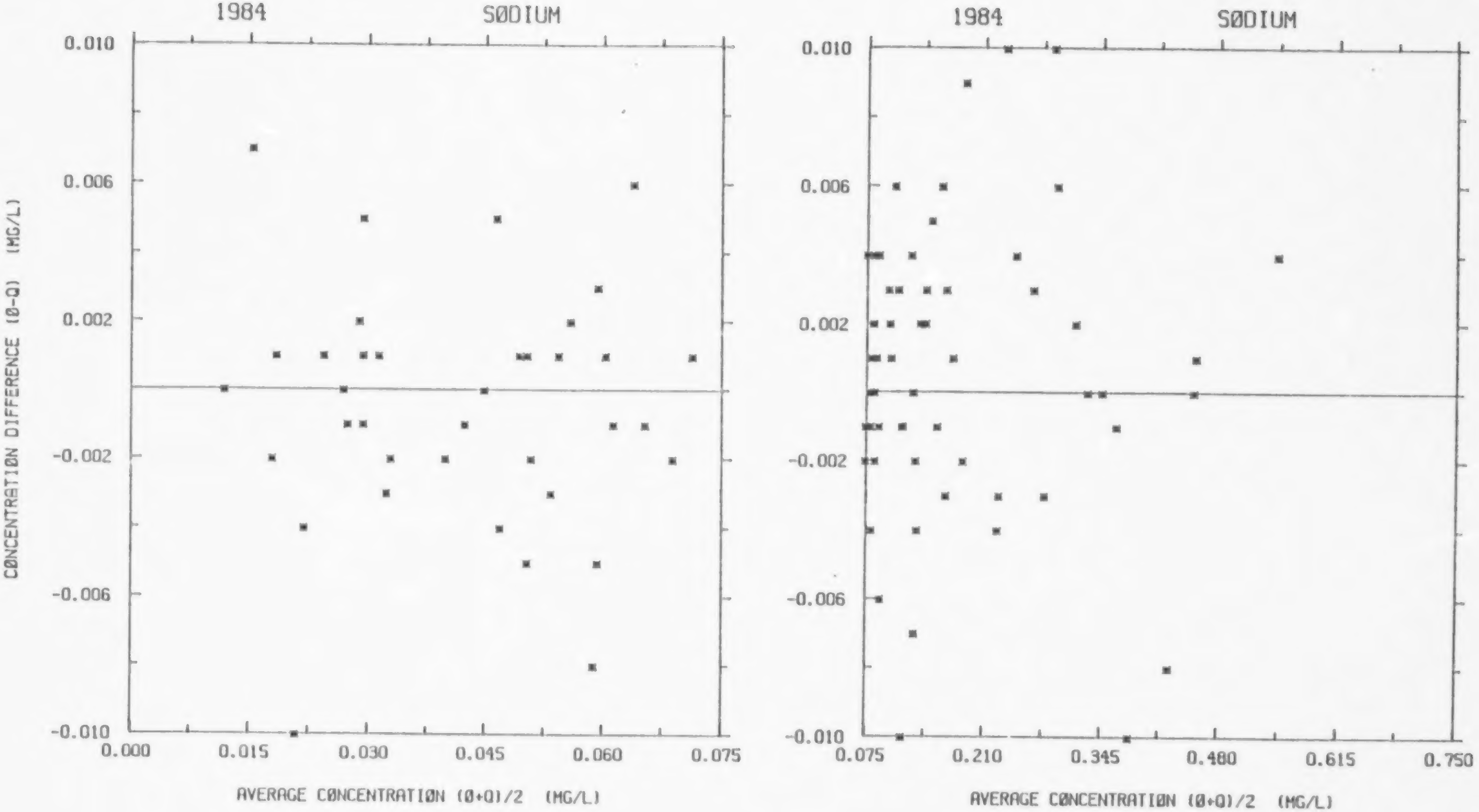


FIGURE 25. O/Q replicate plots for sodium for 1984.

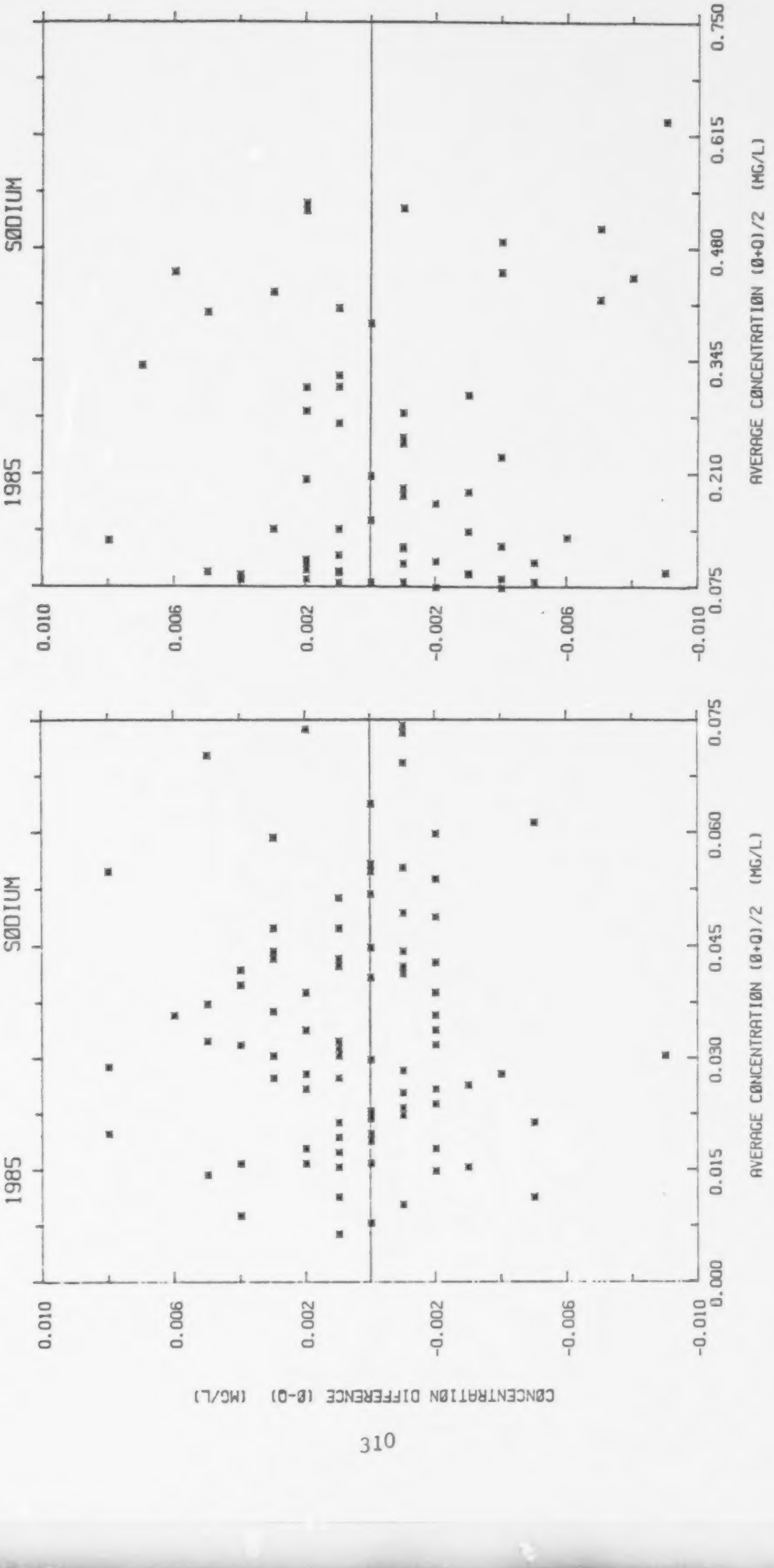


FIGURE 26. O/Q replicate plots for sodium for 1985.

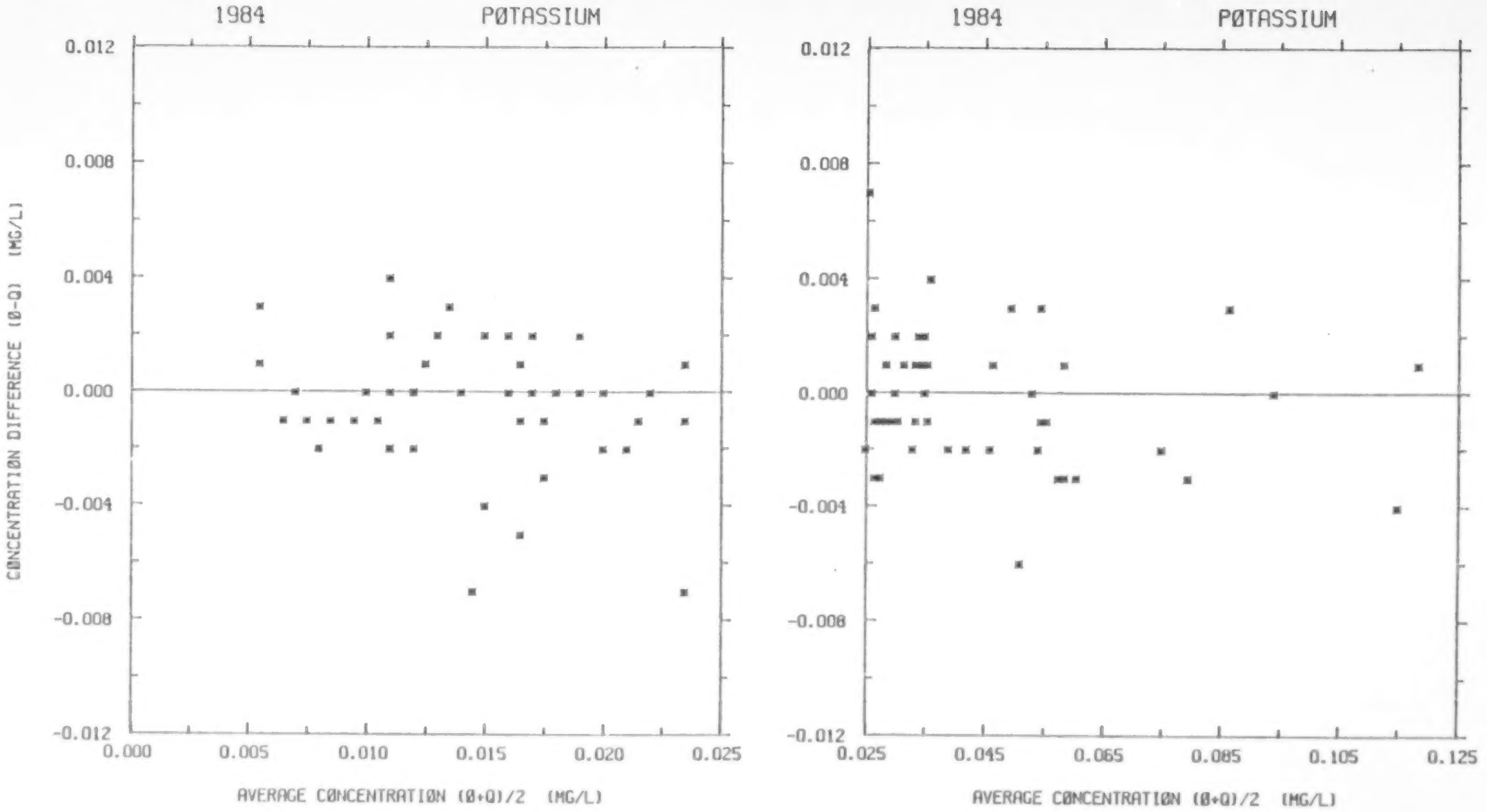


FIGURE 27. O/Q replicate plots for potassium for 1984.

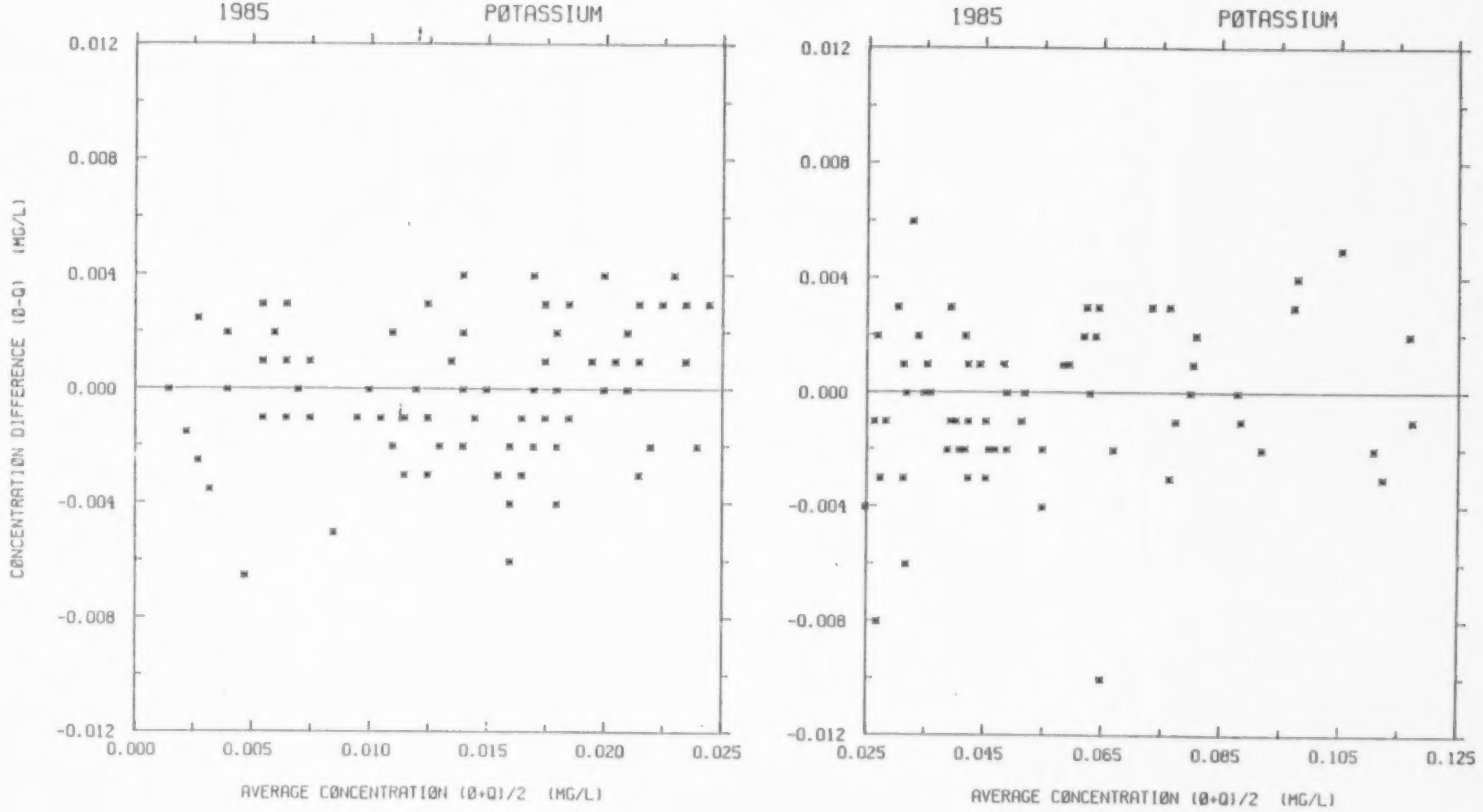


FIGURE 28. O/Q replicate plots for potassium for 1985.

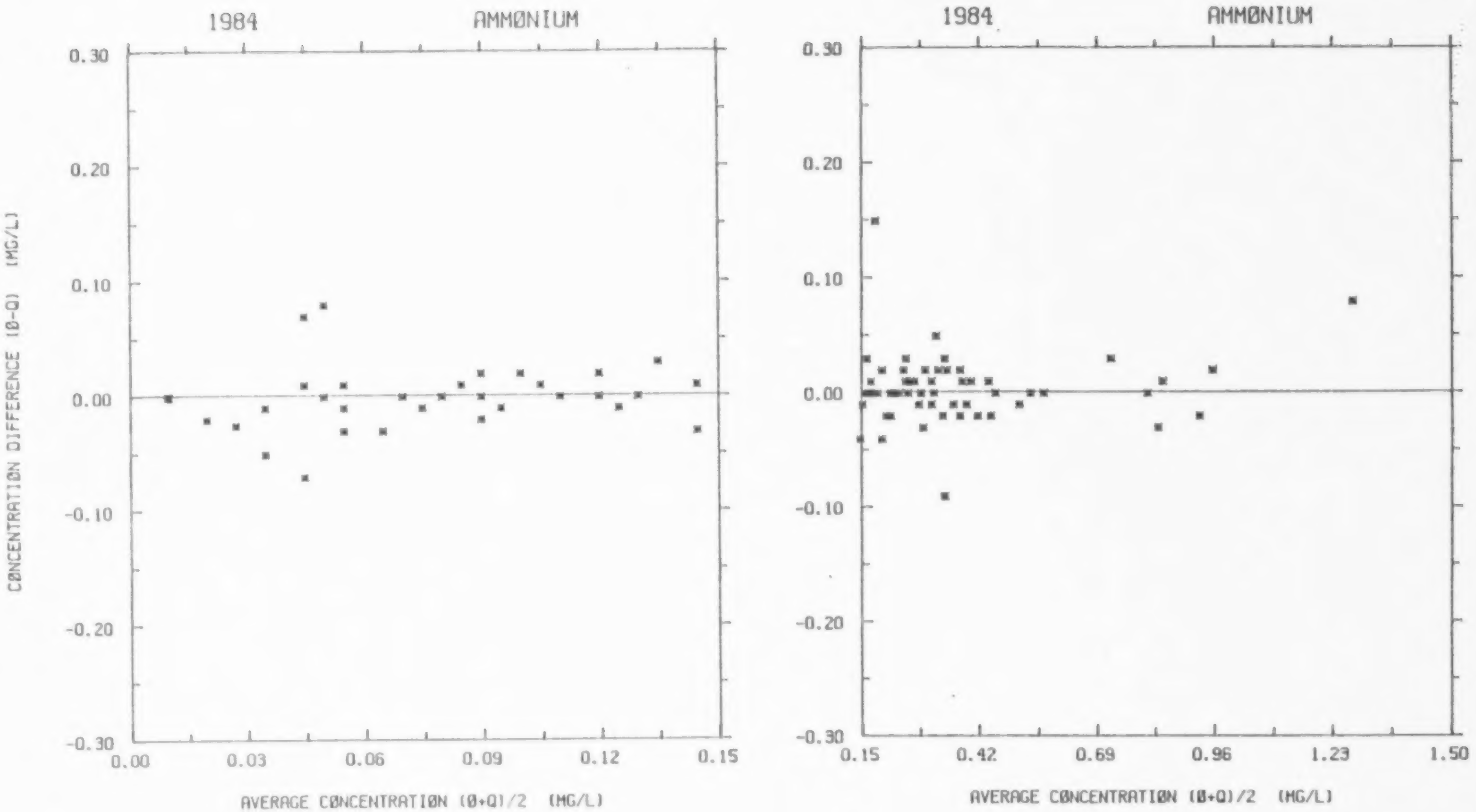


FIGURE 29. O/Q replicate plots for ammonium for 1984.

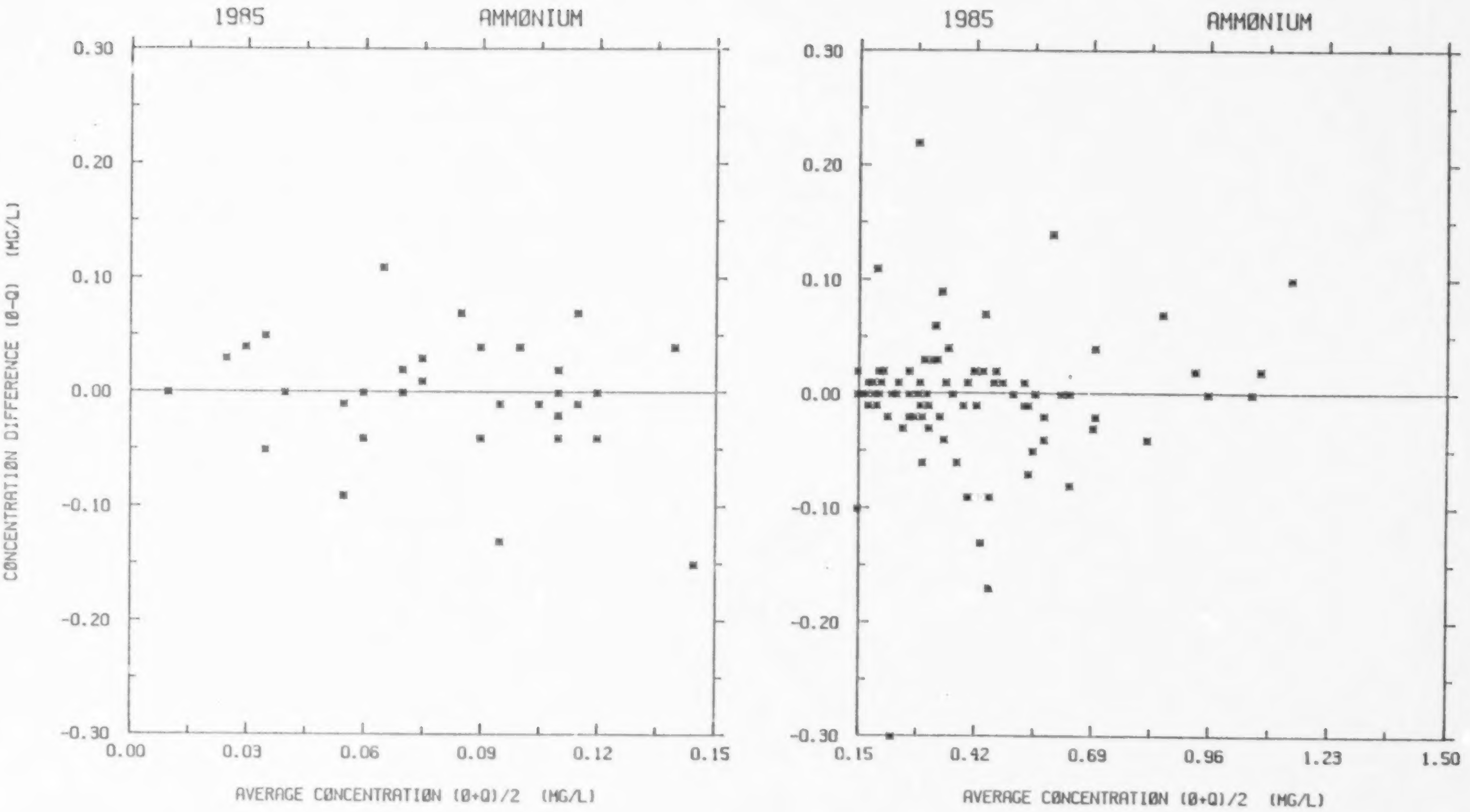


FIGURE 30. O/Q replicate plots for ammonium for 1985.

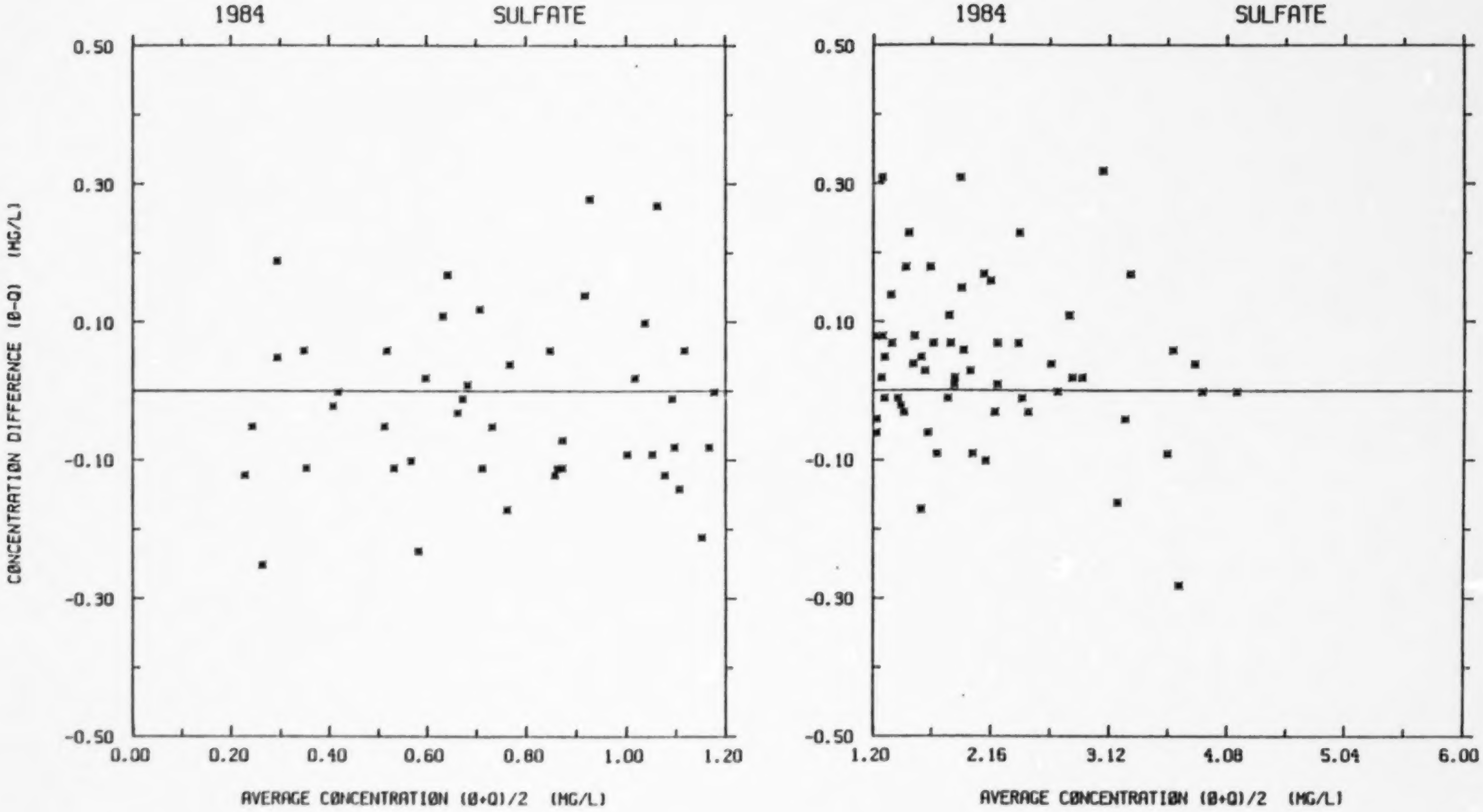


FIGURE 31. O/Q replicate plots for sulfate for 1984.

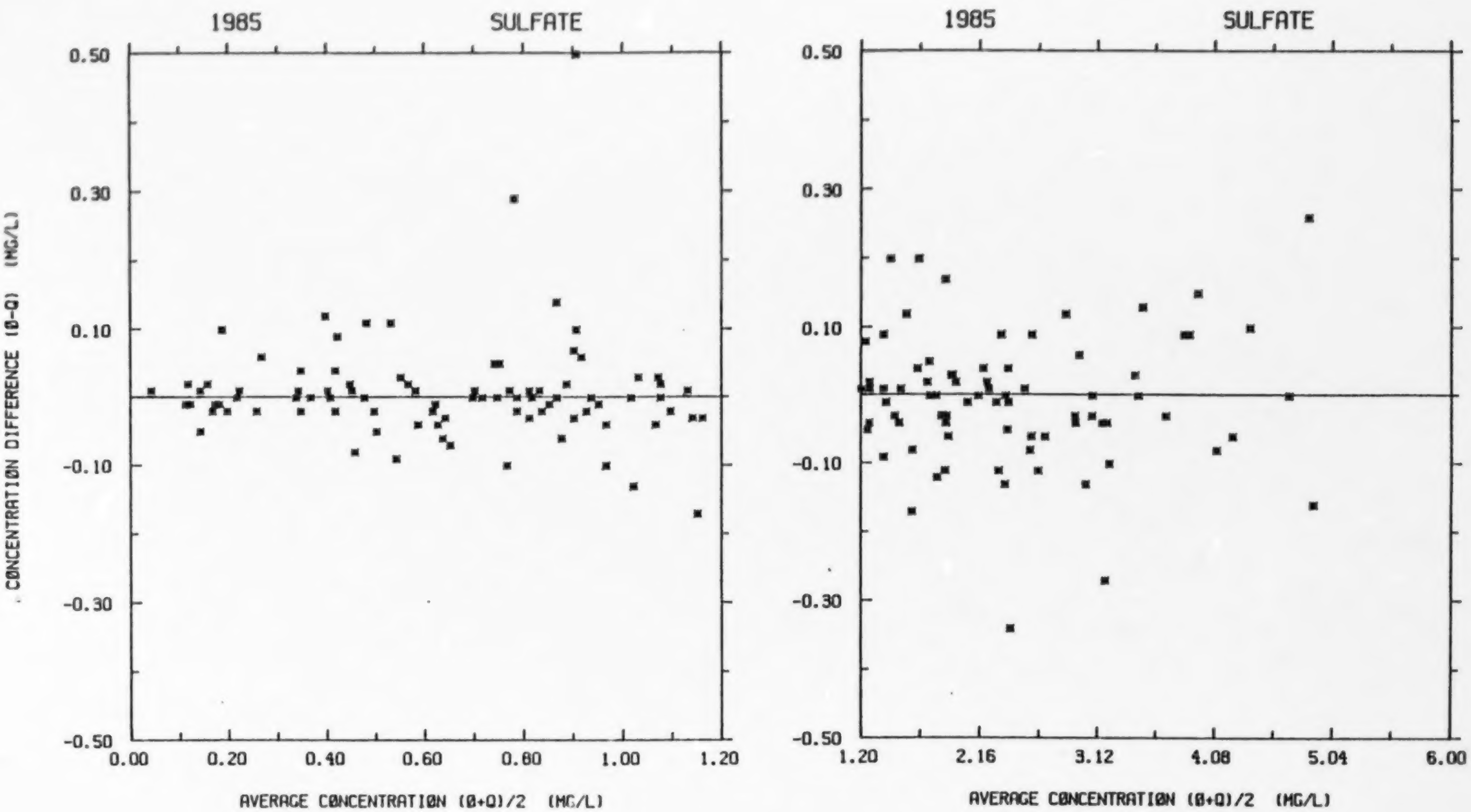


FIGURE 32. O/Q replicate plots for sulfate for 1985.

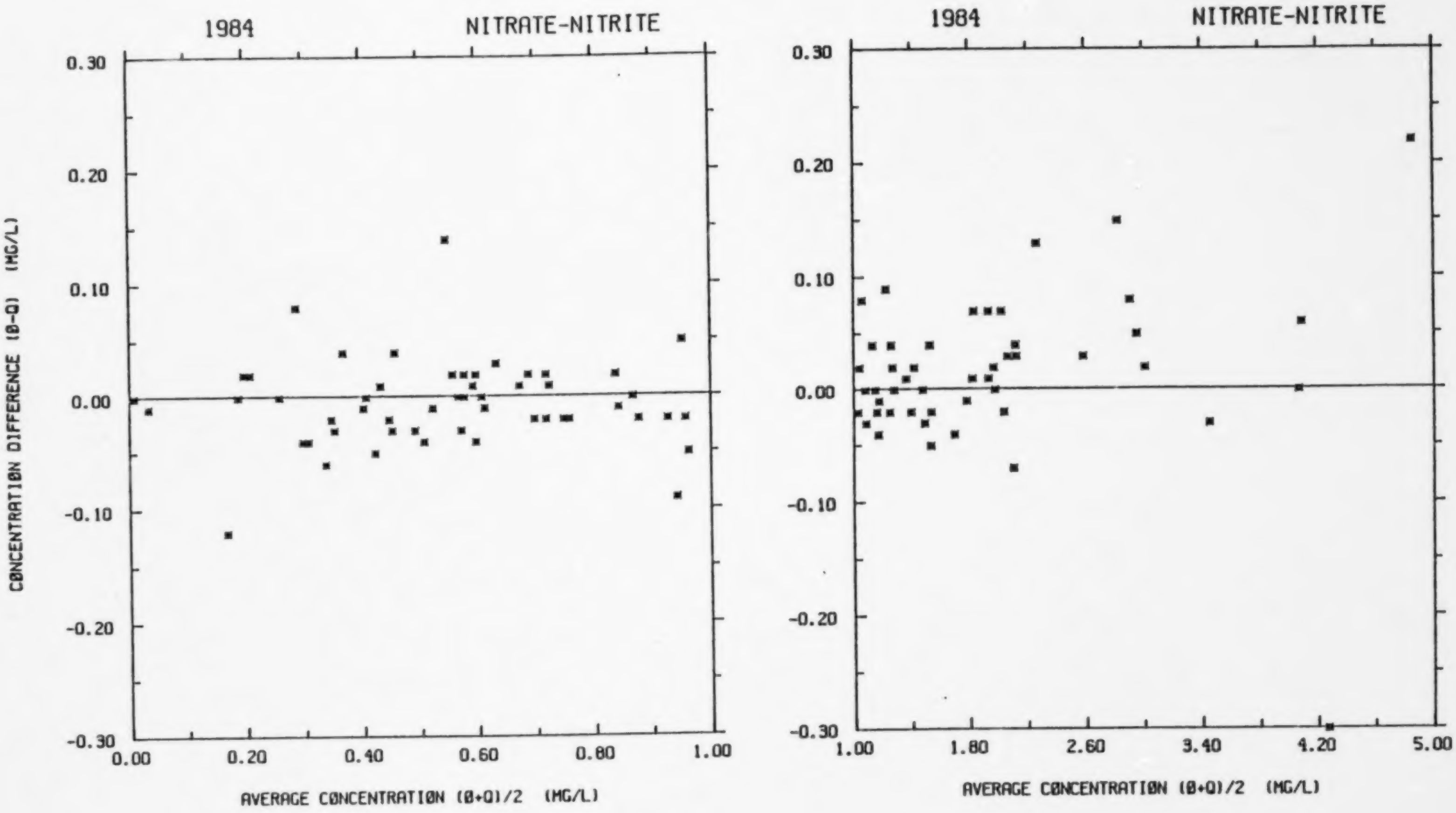


FIGURE 33. O/Q replicate plots for nitrate-nitrite for 1984.

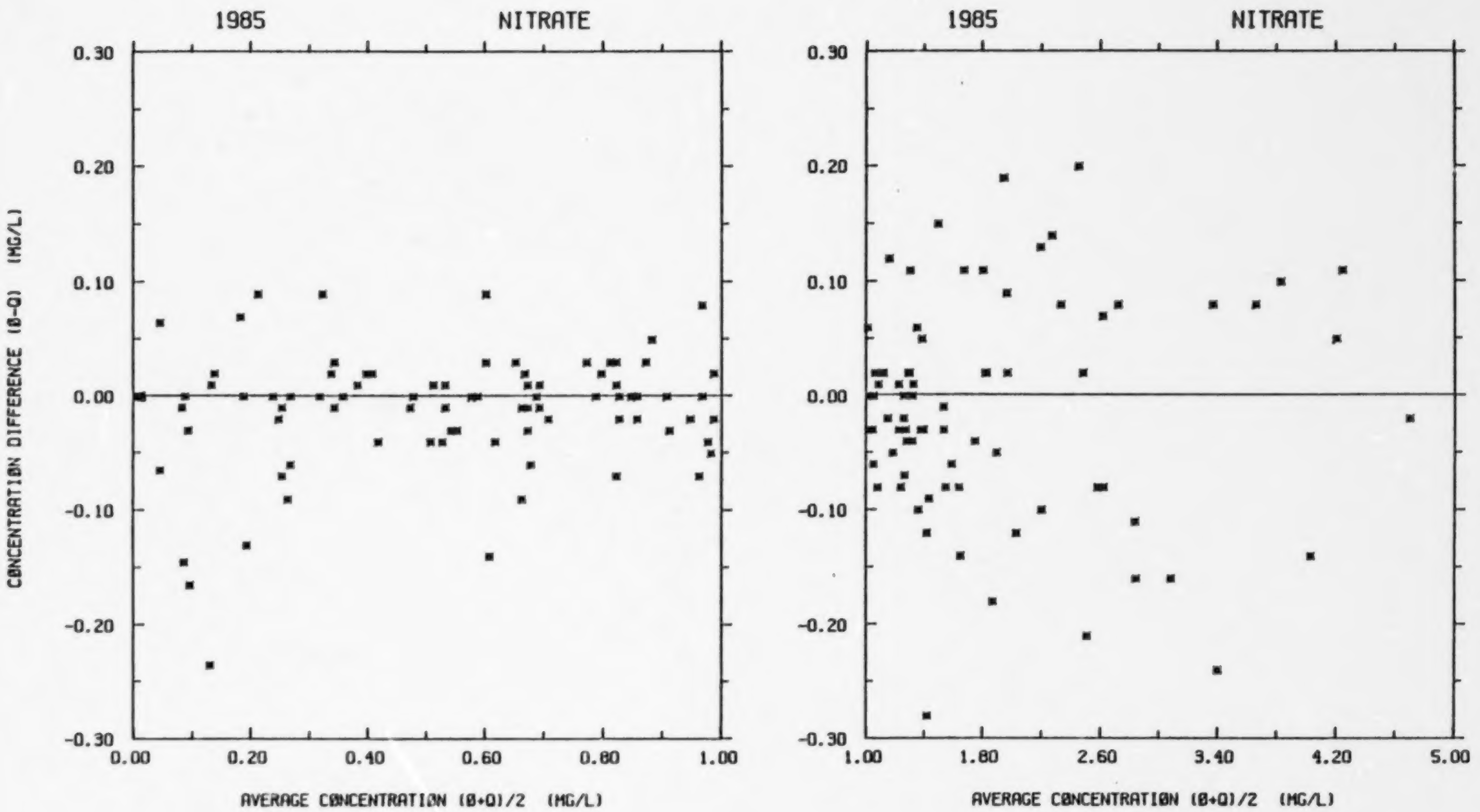


FIGURE 34. O/Q replicate plots for nitrate for 1985.

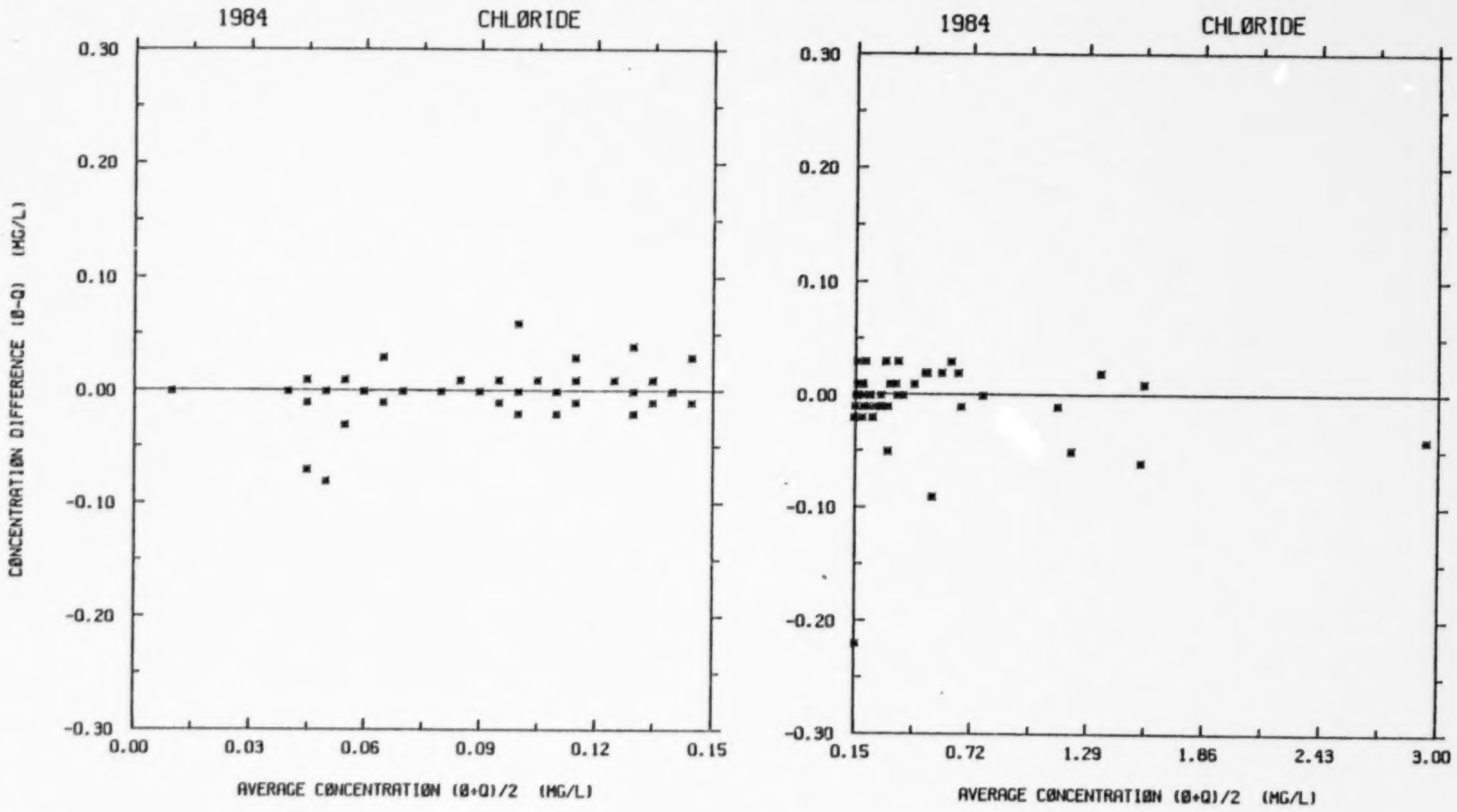


FIGURE 35. O/Q replicate plots for chloride for 1984.

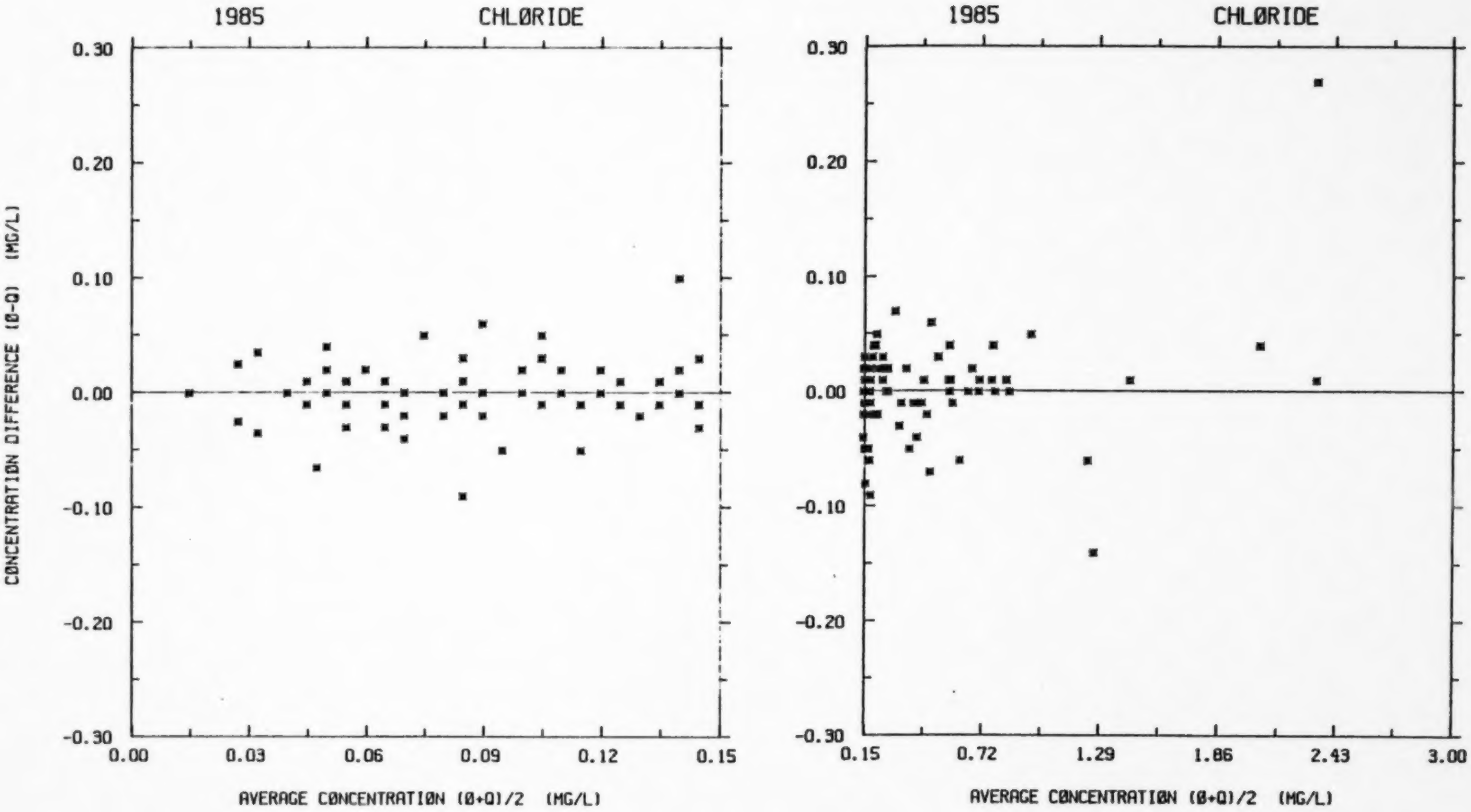


FIGURE 36. O/Q replicate plots for chloride for 1985.

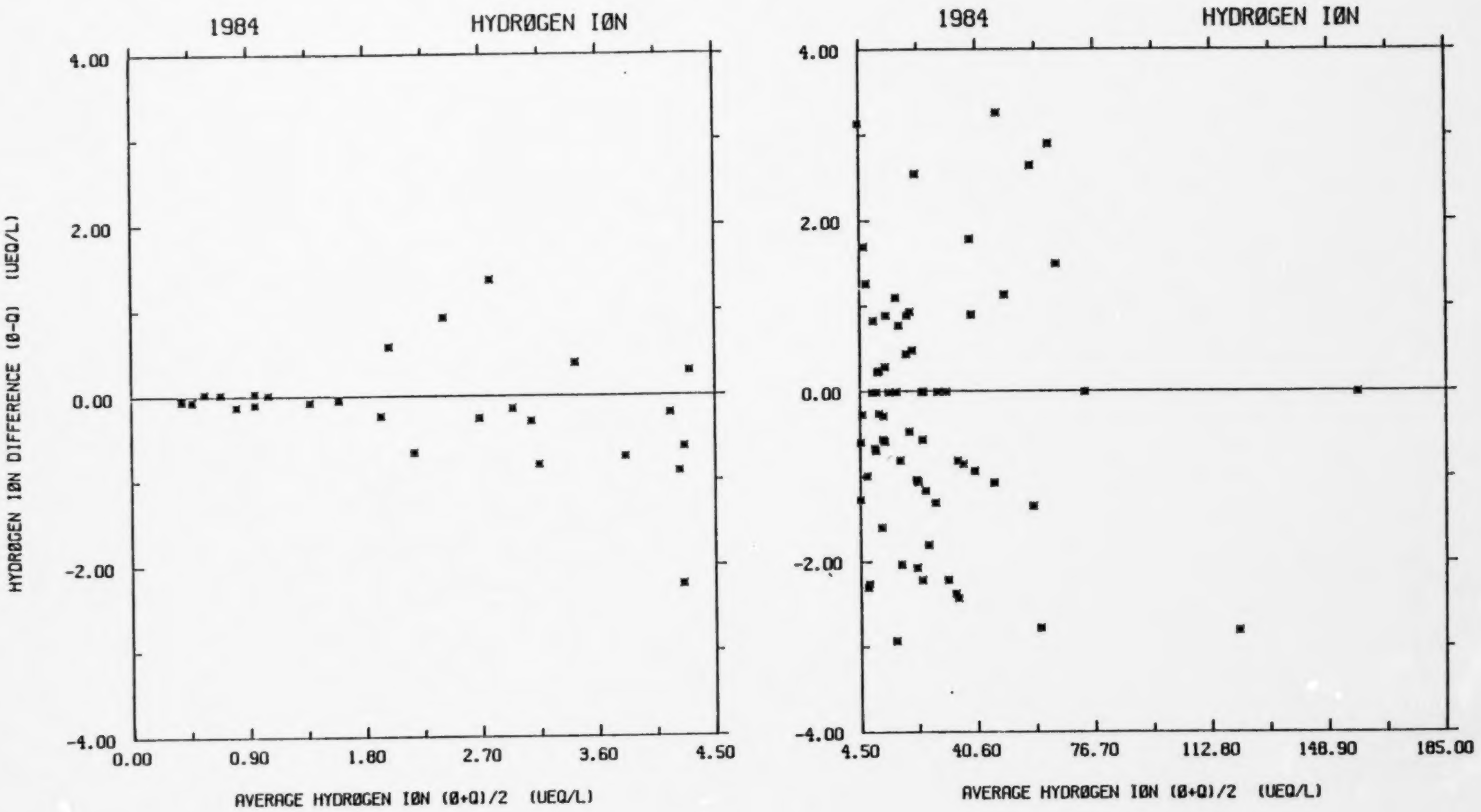


FIGURE 37. O/Q replicate plots for hydrogen ion for 1984.

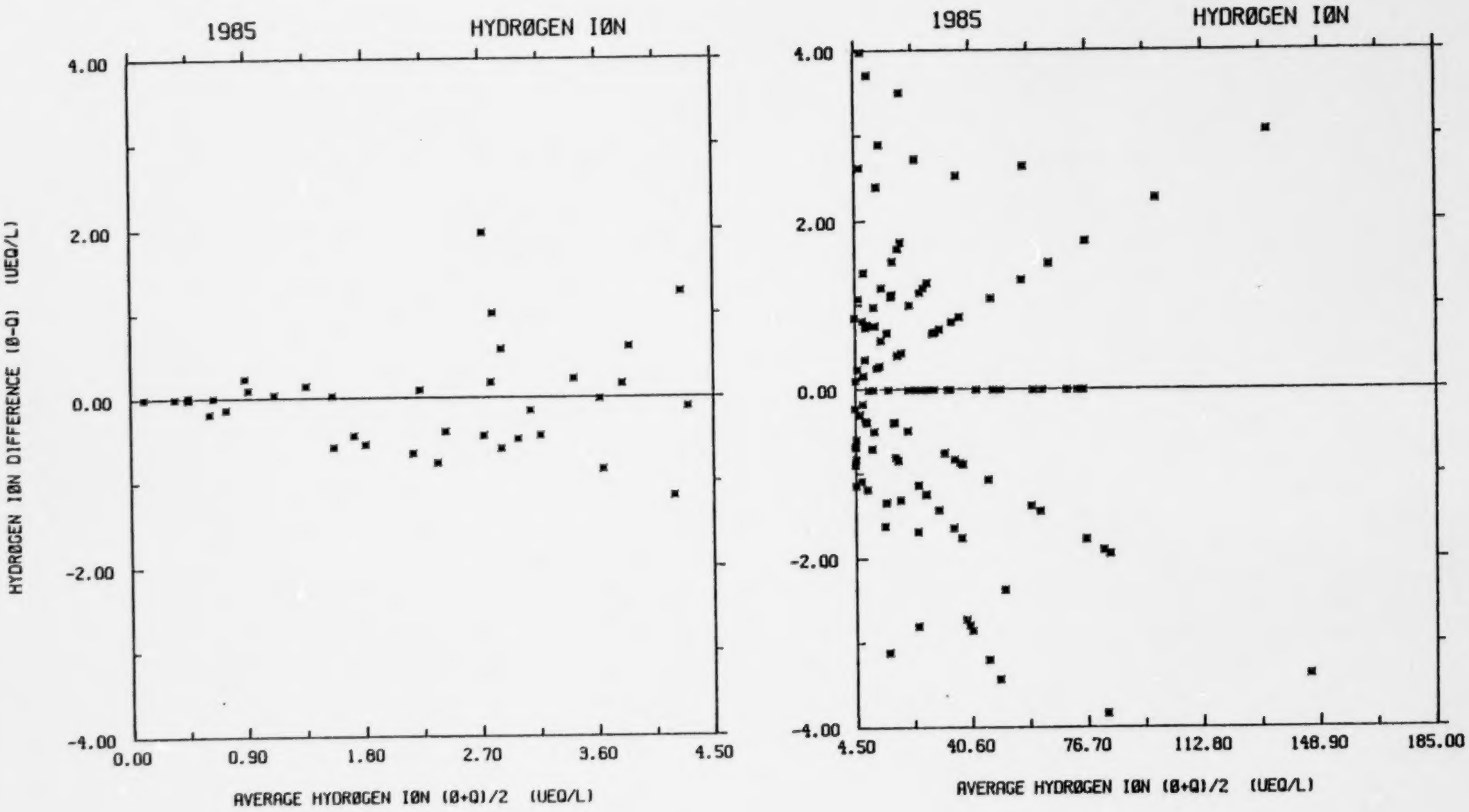


FIGURE 38. O/Q replicate plots for hydrogen ion for 1985.

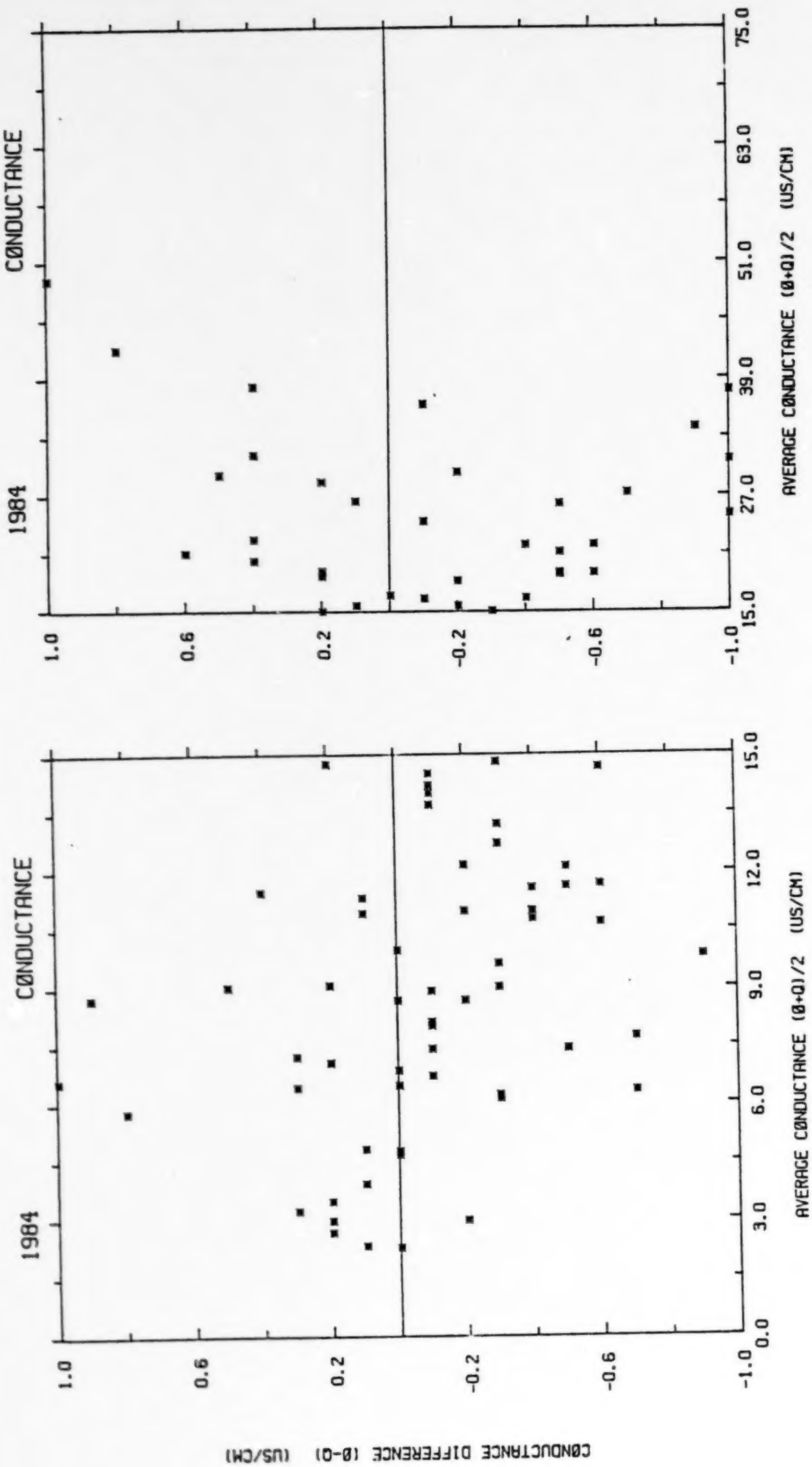


FIGURE 39. O/Q replicate plots for specific conductance for 1984.

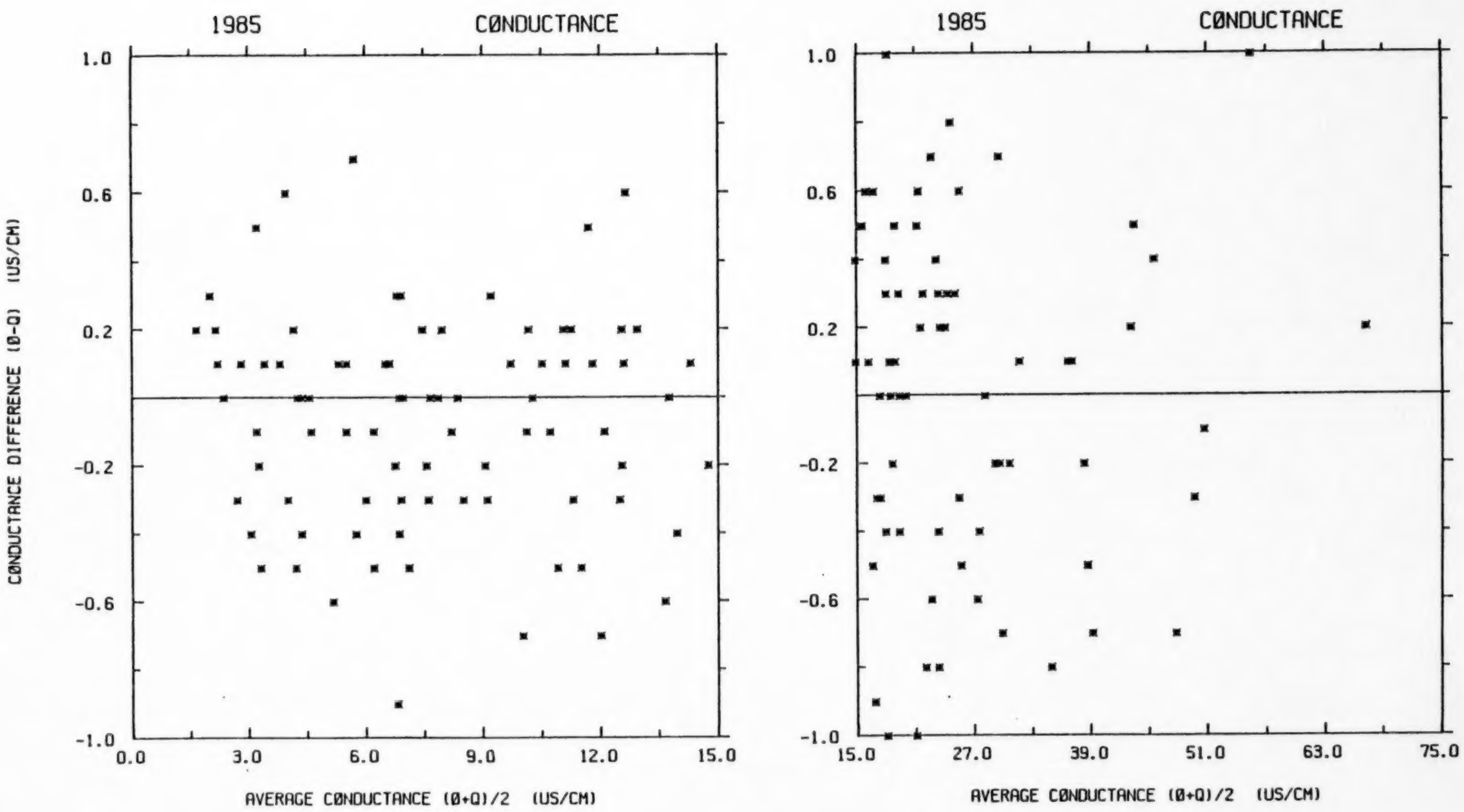


FIGURE 40. O/Q replicate plots for specific conductance for 1985.

TABLE 1 (A-B) Data Summary for Replicate Analysis in 1984.

Parameter	n[a]	Median Difference (mg/L)	Mean Difference (mg/L)	Standard Deviation (mg/L)
Calcium	231	0.001	0.001	0.006
Magnesium	231	0.000	0.000	0.001
Sodium	231	0.000	0.001	0.006
Potassium	231	0.000	0.000	0.001
Ammonium	231	0.00	0.00	0.02
Sulfate	231	0.00	0.01	0.08
Nitrate-Nitrite	231	0.00	0.00	0.03
Chloride	231	0.00	0.00	0.03
pH (units)	231	0.00	0.00	0.02
Specific Conductance (uS/cm)	231	0.0	-0.1	0.2

a. number of replicate pairs

TABLE 2 (O-Q) Data Summary for Replicate Analysis in 1984.

Parameter	n[a]	Median Difference (mg/L)	Mean Difference (mg/L)	Standard Deviation (mg/L)
Calcium	108	-0.001	-0.003	0.034
Magnesium	108	0.000	-0.001	0.009
Sodium	108	0.000	0.007	0.156
Potassium	108	0.000	-0.006	0.059
Ammonium	108	0.00	0.00	0.05
Sulfate	108	0.01	0.01	0.12
Nitrate-Nitrite	108	0.00	0.01	0.12
Chloride	108	0.00	0.01	0.15
pH (units)	108	-0.01	-0.01	0.02
Specific Conductance (uS/cm)	108	-0.1	-0.2	1.2

a. number of replicate pairs

TABLE 3 (A-B) Data Summary for Replicate Analysis in 1985.

Parameter	n[a]	Median Difference (mg/L)	Mean Difference (mg/L)	Standard Deviation (mg/L)
Calcium	177	0.000	0.000	0.003
Magnesium	177	0.000	0.000	0.002
Sodium	177	0.000	0.000	0.005
Potassium	177	0.000	-0.001	0.014
Ammonium	177	0.00	0.00	0.01
Sulfate	177	0.00	-0.01	0.06
Nitrate	177	0.00	-0.01	0.05
Chloride	177	0.00	0.00	0.03
pH (units)	177	0.00	0.00	0.02
Specific Conductance (uS/cm)	177	0.0	0.0	0.4

a. number of replicate pairs

TABLE 4 (O-Q) Data Summary for Replicate Analysis in 1985.

Parameter	n[a]	Median Difference (mg/L)	Mean Difference (mg/L)	Standard Deviation (mg/L)
Calcium	176	0.000	-0.001	0.007
Magnesium	176	0.000	0.000	0.002
Sodium	176	0.000	0.000	0.048
Potassium	176	0.000	0.000	0.012
Ammonium	176	0.00	0.00	0.05
Sulfate	176	0.00	-0.01	0.27
Nitrate	176	0.00	-0.01	0.11
Chloride	176	0.00	0.01	0.08
pH (units)	176	0.00	-0.01	0.02
Specific Conductance (uS/cm)	176	0.0	-0.1	0.7

a. number of replicate pairs

APPENDIX D

Interlaboratory Comparison Data
WMO and LRTAP
1984-1985

TABLE 1 Interlaboratory Comparison of Reference Precipitation Samples - April 1984 - Compares CAL Values to Expected Values.

	Samples					
	1XXX		2XXX		3XXX	
Parameter	CAL	Expected	CAL	Expected	CAL	Expected
Calcium (mg/L)	0.052	0.056	0.010	0.013	0.104	0.115
Magnesium (mg/L)	0.020	0.022	0.010	0.010	0.038	0.040
Sodium (mg/L)	0.185	0.185	0.243	0.241	0.483	0.490
Potassium (mg/L)	0.078	0.066	0.096	0.094	0.097	0.094
Ammonium (mg/L)	0.12	0.107	0.84	0.808	1.09	1.028
Nitrate (mg/L)	0.49	0.496	0.53	0.505	6.95	6.861
Chloride (mg/L)	0.27	0.28	0.40	0.41	1.23	1.26
Sulfate (mg/L)	2.52	2.427	6.14	6.318	10.31	11.028
pH (units)	4.31	4.28	4.03	4.01	3.58	3.55
Specific Conductance (uS/cm)	23.8	24.2	48.5	50.7	129.2	136.2

TABLE 2 Interlaboratory Comparison of Reference Precipitation Samples - October 1984 - Compares CAL Values to Expected Values.

	Samples					
	1XXX		2XXX		3XXX	
Parameter	CAL	Expected	CAL	Expected	CAL	Expected
Calcium (mg/L)	0.048	0.053	0.132	0.133	<0.009	0.005
Magnesium (mg/L)	0.019	0.019	0.010	0.010	0.039	0.038
Sodium (mg/L)	0.190	0.187	0.251	0.246	0.488	0.486
Potassium (mg/L)	0.069	0.067	0.088	0.082	0.101	0.099
Ammonium (mg/L)	0.10	0.097	0.85	0.788	1.11	1.020
Nitrate (mg/L)	0.49	0.509	0.53	0.522	0.58	0.611
Chloride (mg/L)	0.31	0.29	0.64	0.63	0.96	0.92
Sulfate (mg/L)	2.61	2.615	8.09	8.230	11.68	11.034
pH (units)	4.24	4.28	3.86	3.88	3.73	3.73
Specific Conductance (uS/cm)	25.0	24.4	64.1	66.0	90.2	92.7

TABLE 3 Interlaboratory Comparison of Reference Precipitation Samples - April 1985 - Compares CAL Values to Expected Values.

	Samples					
	1XXX		2XXX		3XXX	
Parameter	CAL	Expected	CAL	Expected	CAL	Expected
Calcium (mg/L)	0.049	0.054	0.050	0.057	0.052	0.053
Magnesium (mg/L)	0.019	0.019	0.010	0.010	0.039	0.039
Sodium (mg/L)	0.191	0.194	0.247	0.247	0.400	0.401
Potassium (mg/L)	0.087	0.086	0.080	0.079	0.079	0.080
Ammonium (mg/L)	0.09	0.100	0.82	0.788	1.20	1.153
Nitrate (mg/L)	0.49	0.486	0.49	0.513	7.92	7.959
Chloride (mg/L)	0.39	0.390	0.35	0.376	1.29	1.29
Sulfate (mg/L)	1.77	1.992	6.26	7.115	8.78	10.159
pH (units)	4.40	4.39	4.00	4.00	3.58	3.56
Specific Conductance (uS/cm)	21.2	20.2	54.6	53.1	136.4	134.3

TABLE 4 Interlaboratory Comparison of Reference Precipitation Samples - October 1985 - Compares CAL Values to Expected Values.

	Samples					
	1XXX		2XXX		3XXX	
Parameter	CAL	Expected	CAL	Expected	CAL	Expected
Calcium (mg/L)	0.052	0.050	0.134	0.140	3.68	3.603
Magnesium (mg/L)	0.021	0.020	0.012	0.012	0.362	0.352
Sodium (mg/L)	0.178	0.176	0.244	0.243	0.507	0.504
Potassium (mg/L)	0.071	0.074	0.087	0.090	5.389	5.430
Ammonium (mg/L)	0.12	0.103	0.80	0.808	0.91	0.846
Nitrate (mg/L)	0.62	0.638	0.53	0.520	9.03	8.919
Chloride (mg/L)	0.31	0.290	0.68	0.630	8.63	8.33
Sulfate (mg/L)	2.70	2.52	7.98	7.73	35.0	34.2
pH (units)	4.27	4.29	3.92	3.92	3.20	3.19
Specific Conductance (uS/cm)	26.8	24.7	64.6	51.6	333.5	322.2

TABLE 5 LRTAP Interlaboratory Comparability Study L5 - January 1984 - CAL Reported Values Compared to CCIW Median Values for All Participating Laboratories.[a]

Parameter	Sample Number 5		6		8	
	CAL	CCIW	CAL	CCIW	CAL	CCIW
Calcium (mg/L)	1.00	0.99	1.54	1.5	0.315	0.31
Magnesium (mg/L)	0.212	0.21	0.337	0.33	0.067	0.07
Sodium (mg/L)	0.214	0.21	0.310	0.30	0.518	0.51
Potassium (mg/L)	0.125	0.12	0.148	0.15	0.335	0.32
Nitrate + Nitrite (mg/L)	0.57	0.56	0.78	0.76	0.01	0.009
Chloride (mg/L)	0.63	0.67	0.91	0.90	1.53	1.5
Sulfate (mg/L)	4.84	4.9	5.32	5.4	0.36	0.43
pH (units)	4.38	4.3	4.46	4.4	5.80	5.7
Specific Conductance (uS/cm)	33.3	35.6	35.2	36.5	7.4	8.1

a. number of participating laboratories = 44

TABLE 6 LRTAP Interlaboratory Comparability Study L6 - May 1984 - CAL Reported Values Compared to CCIW Median Values for All Participating Laboratories.[a]

Parameter	Sample Number 1		2		3	
	CAL	CCIW	CAL	CCIW	CAL	CCIW
Calcium (mg/L)	1.51	1.50	2.44	2.42	0.343	0.310
Magnesium (mg/L)	0.336	0.34	0.719	0.73	0.068	0.06
Sodium (mg/L)	0.309	0.31	0.056	0.060	0.581	0.510
Potassium (mg/L)	0.144	0.144	0.091	0.09	0.342	0.33
Nitrate + Nitrite (mg/L)	3.41	3.41	5.00	5.13	0.04	0.04
Chloride (mg/L)	1.00	0.900	0.83	0.795	1.66	1.50
Sulfate (mg/L)	5.28	5.24	5.29	5.20	0.41	0.40
pH (units)	4.40	4.40	4.75	4.79	5.74	5.64
Specific Conductance (uS/cm)	36.9	36.8	33.1	32.5	8.6	8.0

a. number of participating laboratories = 39

TABLE 7 LRTAP Interlaboratory Comparability Study L8 – December 1984 – CAL Reported Values Compared to CCIW Median Values for All Participating Laboratories.[a]

	Sample Number							
	2		4		7		8	
Parameter	CAL	CCIW	CAL	CCIW	CAL	CCIW	CAL	CCIW
Calcium (mg/L)	0.038	0.075	3.11	3.00	1.217	1.22	0.325	0.300
Magnesium (mg/L)	0.716	0.720	0.874	0.900	0.334	0.340	0.069	0.070
Sodium (mg/L)	0.702	0.700	0.162	0.160	0.318	0.320	0.528	0.501
Potassium (mg/L)	1.08	1.075	0.082	0.082	0.691	0.700	0.347	0.330
Nitrate + Nitrite (mg/L)	0.49	0.487	4.51	4.515	1.15	1.107	0.09	0.044
Chloride (mg/L)	0.86	0.900	0.80	0.800	3.28	3.250	1.52	1.500
Sulfate (mg/L)	2.97	3.000	5.63	5.650	3.40	3.400	0.42	0.410
pH (units)	5.11	5.13	6.27	6.19	4.61	4.58	5.74	5.70
Specific Conductance (uS/cm)	18.0	18.20	29.0	30.80	31.1	31.20	8.0	8.00

a. number of participating laboratories = 44

TABLE 8 LRTAP Interlaboratory Comparability Study L9 – May 1985 – CAL Reported Values Compared to CCIW Median Values for All Participating Laboratories.[a]

	Sample Number					
	3		4		5	
Parameter	CAL	CCIW	CAL	CCIW	CAL	CCIW
Calcium (mg/L)	3.06	3.03	1.21	1.23	0.973	0.98
Magnesium (mg/L)	0.865	0.89	0.335	0.34	0.207	0.21
Sodium (mg/L)	0.160	0.16	0.324	0.32	0.222	0.21
Potassium (mg/L)	0.081	0.08	0.700	0.70	0.133	0.13
Ammonium (mg/L)	<0.02	0.013	0.59	0.580	0.58	0.554
Nitrate + Nitrite (mg/L)	4.52	4.47	1.15	1.11	2.39	2.51
Chloride (mg/L)	0.78	0.78	3.24	3.24	0.64	0.62
Sulfate (mg/L)	5.45	5.50	3.30	3.30	4.53	4.80
pH (units)	6.21	6.10	4.61	4.60	4.36	4.33
Specific Conductance (uS/cm)	30.7	30.70	32.4	31.25	35.5	35.00

a. number of participating laboratories = 33

TABLE 9 LRTAP Interlaboratory Comparability Study L10 - August 1985 - CAL Reported Values Compared to CCIW Median Values for All Participating Laboratories.[a]

	Sample Number							
	1		2		3		4	
Parameter	CAL	CCIW	CAL	CCIW	CAL	CCIW	CAL	CCIW
Calcium (mg/L)	13.0	13.00	8.49	8.61	1.497	1.50	7.44	7.35
Magnesium (mg/L)	2.63	2.74	1.83	1.90	0.328	0.332	1.53	1.58
Sodium (mg/L)	1.23	1.22	3.74	3.80	0.311	0.30	1.91	1.90
Potassium (mg/L)	0.491	0.50	0.174	0.17	0.148	0.14	0.617	0.63
Ammonium (mg/L)	<0.02	0.010	<0.02	0.013	0.49	0.477	<0.02	0.010
Nitrate + Nitrite (mg/L)	1.37	1.33	0.04	0.040	3.41	3.32	1.15	1.08
Chloride (mg/L)	1.26	1.24	20.98	21.00	0.94	0.930	2.14	1.94
Sulfate (mg/L)	3.23	3.10	7.62	7.50	5.35	5.29	9.04	8.89
pH (units)	7.78	7.79	5.54	5.60	4.44	4.42	7.43	7.26
Specific Conductance (uS/cm)	95.4	94.85	97.1	95.85	36.3	36.00	64.7	64.00

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a. number of participating laboratories = 42

TABLE 9 (continued) LRTAP Study L10 - August 1985 - CAL Reported Values Compared to CCIW Median Values for All Participating Laboratories.[a]

	Sample Number							
	5		6		7		8	
Parameter	CAL	CCIW	CAL	CCIW	CAL	CCIW	CAL	CCIW
Calcium (mg/L)	3.92	3.92	1.30	1.30	2.38	2.36	0.292	0.289
Magnesium (mg/L)	0.650	0.670	0.274	0.281	0.720	0.730	0.048	0.050
Sodium (mg/L)	0.890	0.915	0.516	0.510	0.133	0.130	0.323	0.310
Potassium (mg/L)	0.402	0.411	0.270	0.270	0.082	0.086	0.155	0.150
Ammonium (mg/L)	<0.02	0.021	<0.02	0.012	0.12	0.124	0.14	0.122
Nitrate + Nitrite (mg/L)	0.58	0.56	0.44	0.41	5.67	5.62	0.62	0.620
Chloride (mg/L)	0.26	0.26	0.25	0.24	0.38	0.37	0.50	0.48
Sulfate (mg/L)	12.79	12.75	5.02	4.91	6.47	6.34	0.35	0.33
pH (units)	6.27	6.10	5.30	5.30	4.48	4.45	6.07	5.90
Specific Conductance (uS/cm)	38.8	39.00	18.1	18.00	40.9	40.00	6.2	6.20

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a. number of participating laboratories = 42

TABLE 9 (concluded) LRTAP Study L10 - August 1985 - CAL Reported Values Compared to CCIW Median Values for All Participating Laboratories.[a]

Parameter	Sample Number 9 CAL	9 CCIW	10 CAL	10 CCIW
Calcium (mg/L)	1.74	1.78	0.275	0.28
Magnesium (mg/L)	0.394	0.40	0.154	0.15
Sodium (mg/L)	0.515	0.50	1.30	1.29
Potassium (mg/L)	0.136	0.14	0.200	0.20
Ammonium (mg/L)	0.04	0.013	0.08	0.070
Nitrate + Nitrite (mg/L)	<0.03	0.031	0.44	0.443
Chloride (mg/L)	0.20	0.20	2.77	2.71
Sulfate (mg/L)	8.21	8.04	1.86	1.84
pH (units)	4.41	4.40	4.54	4.52
Specific Conductance (uS/cm)	36.4	35.60	24.4	24.70

a. number of participating laboratories = 42

TABLE 10 LRTAP Interlaboratory Comparability Study L11 - December 1985 - CAL Reported Values Compared to CCIW Median Values for All Participating Laboratories.[a]

Parameter	Sample Number 1 CAL	1 CCIW	2 CAL	2 CCIW	3 CAL	3 CCIW	4 CAL	4 CCIW
Calcium (mg/L)	2.66	2.630	4.45	4.450	0.978	0.990	0.291	0.280
Magnesium (mg/L)	0.371	0.376	0.714	0.718	0.206	0.210	0.049	0.050
Sodium (mg/L)	0.656	0.653	5.88	5.925	0.219	0.210	0.332	0.320
Potassium (mg/L)	0.243	0.230	0.770	0.780	0.125	0.120	0.154	0.150
Ammonium (mg/L)	<0.02	0.010	<0.02	0.013	0.55	0.534	0.14	0.129
Nitrate + Nitrite (mg/L)	2.77	2.745	0.90	0.908	2.50	2.480	0.61	0.611
Chloride (mg/L)	0.66	0.710	11.04	11.000	0.58	0.622	0.44	0.472
Sulfate (mg/L)	3.42	3.360	7.56	7.475	5.01	4.900	0.36	0.360
pH (units)	6.00	6.00	6.54	6.30	4.33	4.33	6.05	5.92
Specific Conductance (uS/cm)	23.2	22.75	70.0	67.70	36.5	34.05	6.3	6.00

a. number of participating laboratories = 51

TABLE 10 (continued) LRTAP Interlaboratory Comparability Study L11 - December 1985 - CAL Reported Values Compared to CCIW Median Values for All Participating Laboratories.[a]

	Sample Number							
	5		6		7		8	
Parameter	CAL	CCIW	CAL	CCIW	CAL	CCIW	CAL	CCIW
Calcium (mg/L)	2.53	2.510	1.21	1.230	2.39	2.385	5.68	5.670
Magnesium (mg/L)	0.866	0.870	0.336	0.340	0.675	0.680	0.501	0.510
Sodium (mg/L)	0.168	0.160	0.328	0.320	0.578	0.570	0.622	0.620
Potassium (mg/L)	0.080	0.080	0.704	0.700	0.406	0.400	0.236	0.230
Ammonium (mg/L)	<0.02	0.009	0.66	0.656	<0.02	0.023	<0.02	0.013
Nitrate + Nitrite (mg/L)	4.89	4.828	1.18	1.152	1.04	1.062	0.92	0.930
Chloride (mg/L)	0.73	0.783	3.15	3.260	0.35	0.405	0.20	0.240
Sulfate (mg/L)	5.98	5.890	3.48	3.355	8.58	8.510	6.50	6.345
pH (units)	5.03	5.05	4.65	4.67	5.47	5.50	7.17	7.10
Specific Conductance (uS/cm)	32.3	31.30	32.3	31.15	29.5	29.00	40.5	39.00

[a] number of participating laboratories = 51

TABLE 10 (concluded) LRTAP Interlaboratory Comparability Study L11 - December 1985 - CAL Reported Values Compared to CCIW Median Values for All Participating Laboratories.[a]

	Sample Number			
	9		10	
Parameter	CAL	CCIW	CAL	CCIW
Calcium (mg/L)	6.11	6.115	4.23	4.305
Magnesium (mg/L)	1.24	1.27	0.926	0.950
Sodium (mg/L)	0.581	0.580	1.91	1.910
Potassium (mg/L)	0.234	0.230	0.089	0.090
Ammonium (mg/L)	<0.02	0.010	<0.02	0.013
Nitrate + Nitrite (mg/L)	0.60	0.620	<0.03	0.044
Chloride (mg/L)	0.52	0.560	10.77	10.70
Sulfate (mg/L)	1.51	1.470	3.89	3.750
pH (units)	7.54	7.44	5.57	5.64
Specific Conductance (uS/cm)	45.7	44.45	50.2	49.65

[a] number of participating laboratories = 51

SECTION 11
NADP/NTN Quality Assurance and Related Publications

no.	Type	Publication
FIELD SITE OPERATIONS:		
1.	SOP	Semonin and Volchok, 1979. **Site Selection and Certification, North Central Regional Project NC-141:Atmospheric Deposition** (National Atmospheric Deposition Program).
2.	SOP	Bigelow, 1984. **Instruction Manual: NADP/NTN Site Selection and Installation.**
3.	SOP	Semonin and Volchok, 1978. **Field Observer Instruction Manual, North Central Regional Project NC-141:Atmospheric Deposition** (National Atmospheric Deposition Program).
4.	SOP	Bigelow, 1982. **Instruction Manual: Site Operation.**
5.	SOP	Bigelow and Dossett, 1988. **Instruction Manual: Site Operation.**
6.	SOP	Dossett, 1984. **Aerochem Metrics Precipitation Collector Maintenance Manual.**
7.	SOP	Eaton and Tew, 1985. **Work Plan for Quality Assurance Assistance to The National Atmospheric Deposition Program and The National Trends Network Deposition Monitoring Program.**
8.	SOP	Stensland et al., 1983. **NADP Quality Control Procedures for Wet Deposition Sample Collection and Field Measurements.**
9.	Report	Stensland and Bowersox, 1982. **Evaluation of Dry Wet-Side NADP Samples.**
10.	Report	Schroder et al., 1985. **Comparison of Daily and Weekly Precipitation Sampling Efficiencies Using Automatic Collectors.**
11.	Report	Bigelow, 1986. **Quality Assurance Report: NADP/NTN Deposition Monitoring; Field Operations.**
12.	Report	Eaton et al, 1987. **Summary Report For The National Atmospheric Deposition Program/ National Trends Network (NADP/NTN) Site Visitation Program, For The Period December 1984 through September 1986.**
13.	Report	Schroder and Brennan, 1985. **Precision Of The Measurement Of pH And Specific Conductance At National Atmospheric Deposition Program Monitoring Sites, October 1981-November 1983.**
14.	Report	Schroder et al, 1987. **Results Of Intercomparison Studies For The Measurement Of pH And Specific Conductance At National Atmospheric Deposition Program National Trends Network Monitoring Sites, October 1981-October 1985.**
LABORATORY OPERATIONS:		
15.	SOP	Peden et al., 1979. **Precipitation Sample Handling, analysis, And Storage.**
16.	SOP	Peden et al., 1986. **Methods For The Collection And Analysis Of Precipitation.**
17.	Report/ SOP	National Atmospheric Deposition Program, 1980. **NADP Quality Assurance Report, Central Analytical Laboratory, Jan 1 1979 to Dec 31 1979.**
18.	Report	Peden, 1983. **Sampling, Analytical, And Quality Assurance Protocols For The National Atmospheric Deposition Program.** Sampling and Analysis Of Rain.
19.	Report	Lockard, 1987. **Quality Assurance Report: NADP/NTN Deposition Monitoring, Laboratory Operations, Central Analytical Laboratory, 1978 through 1983.**
20.	Report	Lockard, 1988. **Quality Assurance Report: NADP/NTN Deposition Monitoring, Laboratory Operations, Central Analytical Laboratory, 1984-1985.**
21.	Report	Brooks, et al, 1985. **Interlaboratory Comparability, Bias, and Precision For Four Laboratories Measuring Constituents In Precipitation, November 1982-August 1983.**
22.	Report	Brooks, et al, 1987. **Interlaboratory Comparability, Bias, and Precision For Four Laboratories Measuring Constituents In Precipitation, November 1982-August 1983.**

no.	Type	Publication
DATA MANAGEMENT:		
23.	SOP	Bowersox, 1985. **Data Validation Procedures for Wet Deposition Samples at the Central Analytical Laboratory of the National Atmospheric Deposition Program.**
24.	Report	Stensland and Bowersox, 1985. **Quality Assurance In Acid Precipitation Monitoring Through The Use Of Ion Balance Calculations.**
OVERALL PROGRAM QUALITY ASSURANCE:		
25.	SOP	Cowling et al., 1977. **Plan Of Research For NC-141 North Central Regional Project On Atmospheric Deposition: Chemical Changes In Atmospheric Deposition And Effects On Agricultural And Forested Land And Surface Waters In The United States.**
26.	SOP	Robertson and Wilson, 1985. **Design of the National Trends Network for Monitoring the Chemistry of Atmospheric Precipitation.**
27.	SOP	NADP Quality Assurance Steering Committee, 1984. **The NADP Quality Assurance Plan.**
28.	SOP	Schroder and Malo, 1985. **Quality Assurance Program For Wet Deposition Sampling And Chemical Analysis For the National Trends Network.**
29.	Report	Schroder et al., 1985. **Precision And Bias Of Selected Analytes Reported By The National Atmospheric Deposition Program And The National Trends Network--January 1980 Through September 1984.**
30.	Report	Schroder et al., 1986. **Quality Assurance Results For Field pH And Specific Conductance Measurements And For Laboratory Analysis, National Atmospheric Deposition Program and National Trends Network--January 1980-September 1984.**
31.	Report	Brooks et al., 1987. **Bias and Precision of Selected Analytes Reported by the National Atmospheric Deposition Program and National Trends Network, 1984.**
32.	Report	Brooks et al., 1987. **Results of External Quality Assurance Program For The National Atmospheric Deposition Program and National Trends Network During 1985.**
33.	Report	See et al., 1988. **External Quality Assurance Results For The National Atmospheric Deposition Program and National Trends Network During 1986.**